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The publications include the *Journal*, containing papers communicated to the Society, the *Abstracts*, covering the current literature in pure Chemistry, the *Indexes*, and the *Annual Reports* on the progress of Chemistry.

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List of Physico-chemical Symbols adopted by the Chemical Society.
[See J.C.S., 1921, **119**, 502—512.]

1. *Mathematical Symbols.*

	Usual symbol.	Alternative symbol.
Base of natural (Napierian) logarithms ...	e	
Diameter	d	
Radius	r	
Ratio of circumference to diameter	π	
Summation.....	Σ	
Variation	δ	
Total differential	d	
Partial differential	∂	

2. *Universal Constants.*

Acceleration due to gravity.....	g	
Mechanical equivalent of heat	J	
Avogadro's constant [number of molecules in 1 gram-molecule (mole)]	N	
Gas constant per mole	R	
Faraday's constant (number of coulombs per gram-equivalent of an ion)	F	
Charge on an electron	e	

3. *General Physics and Chemistry.*

Length	l	
Height.....	h	
Mass	m	
Time	t	
Volume	v, V	
Density (mass per unit volume)	d	D
Pressure	p, P	
Concentration	c, C	
Mole fraction	x	
Critical constants: pressure, volume, temperature (centigrade), temperature (absolute), density	p_c, v_c t_c, T_c d_c	
Reduced quantities: pressure, volume, temperature, density	p_r, v_r t_r, T_r, d_r	
van der Waals's constants	a, b	
Fluidity	ϕ	
Viscosity	η	
Surface tension	γ	σ
Diffusion coefficient	Δ	
Atomic weight	A	
Molecular weight	M	
Velocity coefficient of reaction	k	
Equilibrium constant	$K, (K_c, K_p)$	
van't Hoff coefficient	i	
Degree of dissociation (electrolytic, thermal, etc.)	α	

4. *Heat and Thermodynamics.*

	Usual symbol.	Alternative symbol.
Temperature (centigrade)	t	θ
Temperature (absolute)	T	
Critical temperature	t_c, T_c	
Reduced temperature	t_r, T_r	
Critical solution temperature	t_{cs}, T_{cs}	
Quantity of heat	Q	
Entropy	S	
Specific heat	c	
Specific heat at constant pressure	c_p	
Specific heat at constant volume	c_v	
Ratio of specific heats, $c_p : c_v$	γ	
Molecular heat	C	
Molecular heat at constant pressure	C_p	
Molecular heat at constant volume	C_v	
Latent heat per gram	l	
Latent heat per mole	L	
Maximum work (diminution of free energy)	A	

5. *Optics.*

Wave-length of light	λ	
Refractive index	n	n_r
Specific refractive power (Gladstone and Dale)	r_G, $[r_G]_\lambda^t$	
Specific refractive power (Lorentz and Lorenz)	r_L, $[r_L]_\lambda^t$	
Molecular refractive power	R_G, R_L $[R_G]_\lambda^t$, $[R_L]_\lambda^t$	
Angle of optical rotation	α	
Specific rotatory power	$[\alpha]$	
Molecular rotatory power	$M[\alpha]$	
Specific magnetic rotation	$[\omega]$	
Molecular magnetic rotation	$M[\omega]$	

6. *Electricity and Magnetism.*

Quantity of electricity	Q	
Current intensity	I	
Resistance	R	W
Electromotive force	E	
Electrode potential, or discharge potential of an ion	E	ϵ
Electrode potential referred to the normal hydrogen or normal calomel electrode respectively, the potential of which is taken as zero	E_h, E_c	ϵ_h, ϵ
Normal potential, *i.e.*, the electrode potential referred to the normal hydrogen or normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration	${}_0E_h$, ${}_0E_c$	${}_0\epsilon_h$, ${}_0\epsilon$
Dielectric constant	ϵ	
Conductivity (specific conductance)	κ	
Equivalent conductivity	Λ	
Equivalent conductivity at different dilutions—volumes in litres containing 1 gram-equivalent	Λ_{10}, Λ_v, Λ_∞	

6. *Electricity and Magnetism*—(continued).

	Usual symbol.	Alternative symbol.
Equivalent conductivity of kation and of anion	Λ_k, Λ_a	
Equivalent conductivity of specified ions	Λ_K, Λ_{Cl}	
Molecular conductivity	μ	
Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.	U_k, U_a	
Transport number of kation and of anion	n_k, n_a	
Magnetic permeability	μ	
Magnetic susceptibility	κ	

List of Symbols, Arranged Alphabetically.

Symbol.	Name of quantity.
A	Atomic weight; maximum work.
a	Van der Waals's constant.
b	Van der Waals's constant.
C	Concentration; molecular heat.
c	Concentration; specific heat.
C_p, C_v	Molecular heat at constant pressure, and at constant volume.
c_p, c_v	Specific heat at constant pressure, and at constant volume.
D	Alternative symbol for density.
d	Diameter; total differential; density.
d_c	Critical density.
δ	Reduced density.
E	Electromotive force; electrode potential.
e	Base of Napierian logarithms; charge on an electron.
E_h, E_c	Electrode potential referred to the normal hydrogen or the normal calomel electrode, respectively, the potential of which is taken as zero.
${}_0E_h$, ${}_0E_c$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration.
F	Faraday's constant (number of coulombs per gram-equivalent of an ion).
g	Acceleration due to gravity.
h	Height.
I	Current.
i	Van't Hoff's coefficient.
J	Mechanical equivalent of heat.
K	Equilibrium constant.
K_c, K_p	Equilibrium constant, when molar concentrations and partial pressures respectively are employed.
k	Velocity coefficient of reaction.
L	Latent heat per mole.
l	Length; latent heat per gram.
M	Molecular weight.
$M[\alpha]$	Molecular rotatory power.
$M[\omega]$	Molecular magnetic rotatory power.
m	Mass.
N	Avogadro's constant (Loschmidt's number) or number of molecules in 1 gram-molecule.
n	Refractive index.

List of Symbols, Arranged Alphabetically—(continued).

Symbol.	Name of quantity.
n_k, n_a	Transport number of kation and of anion.
n_r	Refractive index (alternative symbol).
P	Pressure.
p	Pressure.
p_c, p_r	Critical pressure : reduced pressure.
Q	Quantity of heat; quantity of electricity.
R	Gas constant per mole; electrical resistance.
R_G, R_L	Molecular refractive power, according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
r	Radius.
r_G, r_L	Specific refractive power according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
S	Entropy.
T	Absolute temperature.
T_c	Critical temperature (on the absolute scale).
T_r	Reduced temperature (absolute).
T_{cs}	Critical solution temperature (absolute).
t	Time; temperature (centigrade).
t_c	Critical temperature (centigrade).
t_{cs}	Critical solution temperature (centigrade).
t_r	Reduced temperature (centigrade).
U_k, U_a	Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.
V	Volume.
v	Volume.
v_c, v_r	Critical volume : reduced volume.
W	Electrical resistance (alternative symbol).
x	Mole fraction.
α	Degree of dissociation (electrolytic, thermal, etc.); angle of optical rotation.
$[\alpha]$	Specific rotatory power.
γ	Surface tension; ratio of specific heats.
Δ	Diffusion coefficient.
δ	Variation.
∂	Partial differential.
ϵ	Electrode potential (alternative symbol); dielectric constant.
ϵ_h, ϵ	Electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, the potential of which is taken as zero (alternative symbols).
${}^0\epsilon_h$, ${}^0\epsilon$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration (alternative symbols).
η	Viscosity.
θ	Temperature (centigrade), (alternative symbol).
κ	Specific conductance (conductivity); magnetic susceptibility.
Λ	Equivalent conductivity.
$\Lambda_{1\theta}$, Λ_v, Λ_∞	Equivalent conductivity at different dilutions (volumes in litres containing 1 gram-equivalent).
Λ_k, Λ_a	Equivalent conductivity of kation and of anion.
λ	Wave-length of light.
μ	Molecular conductivity; magnetic permeability.
π	Ratio of circumference to diameter.
Σ	Summation.
σ	Surface tension (alternative symbol).
ϕ	Fluidity.
$[\omega]$	Specific magnetic rotation.

JOURNAL

OF

THE CHEMICAL SOCIETY.

I.—*The Action of Hydrogen Sulphide on a Neutral Solution of Potassium Permanganate.*

By Horace Barratt Dunnicliff and Sukh Dayal Nijhawan.

When a slow current of hydrogen sulphide is passed through a 1% solution of potassium permanganate, the purple solution becomes brown and a white deposit of sulphur appears round the delivery tube. After a short time, a greyish-brown solid separates without appreciable rise in temperature; this slowly changes first to a yellow mixture of hydrated manganese dioxide, manganese sulphide, and sulphur and finally to a pink precipitate of manganese sulphide containing much sulphur, the temperature rising rather more than 10°.

The course of the reaction was investigated in stages.

When a solution of potassium permanganate was shaken with hydrogen sulphide solution, a brownish-black precipitate of hydrated manganese dioxide and sulphur formed immediately; the faintly alkaline filtrate contained unchanged permanganate. The precipitate was well washed by decantation with air-free water, and the manganese dioxide in it was estimated by determining the amount of chlorine it liberated from hydrochloric acid. The liquid left over from this estimation was treated with sodium carbonate, and the total manganese weighed as Mn_3O_4. Three estimations gave values of 1 : 3·8, 1 : 3·1, and 1 : 2·7 for the molecular ratio $MnO : MnO_2$, showing that the manganese is only partly precipitated as hydrated dioxide.

Through solutions of potassium permanganate of various concentrations hydrogen sulphide was passed until the whole of the manganese was converted into sulphide. The precipitate was filtered off, and the manganese present in it as sulphide was estimated by two methods: (1) The sulphide was extracted with dilute hydrochloric acid, the solution filtered, and the manganese precipitated

as carbonate and weighed as Mn_3O_4. Recovery = 99·8% of theory. (2) The sulphide containing free sulphur was ignited and so converted into Mn_3O_4. Recovery = 99·9% of theory.

The yellow filtrate, which contained colloidal sulphur and was faintly alkaline to phenolphthalein, was freed from hydrogen sulphide by shaking under reduced pressure, and kept in a vacuum desiccator. The sulphur deposited was filtered off and the liquor, now colourless, was left in a vacuum desiccator over a dehydrating agent for some days. Needle-shaped crystals of potassium thiosulphate and rhombic crystals of potassium sulphate grew in it as it became concentrated. The filtrate did not contain polythionates, sulphide, or sulphite. To test for polythionates, the filtrate was examined qualitatively by the tests given by Takamatsu and Smith (J., 1880, **37**, 592), Bassett and Durrant (J., 1923, **123**, 1279), Gutmann (*Ber.*, 1905, **38**, 3277; 1907, **40**, 3614), Sander (*Z. angew. Chem.*, 1915, **28**, 9; 1916, **29**, 11, 16), and Riesenfeld and Feld (*Z. anorg. Chem.*, 1921, **119**, 225) in comparison with control thionate solutions of known concentrations.

It was shown that hydrogen sulphide has no action on thiosulphates by passing the gas through standard solutions of sodium thiosulphate at various temperatures; the excess was removed under diminished pressure, and the solutions were titrated against iodine solution. The absence of colloidal sulphur was demonstrated by negative results on the addition of electrolytes and with the cataphoresis test.

Estimation of the Compounds produced at Various Stages in the Action of Hydrogen Sulphide on Potassium Permanganate.

In all cases, the excess of hydrogen sulphide was removed by means of a suction pump or by the addition of lead carbonate.

(1) *Estimation of the Products of the Complete Reaction.*—The manganese is quantitatively precipitated as sulphide (see above).

The sulphate in the filtrate was estimated as barium sulphate, the precautions advised by Taylor (*J. Soc. Chem. Ind.*, 1923, **42**, 294T) being taken but acetic acid being used instead of hydrochloric acid as suggested by Müller (*Bull. Soc. chim.*, 1916, **19**, 8) when sulphates are being estimated in presence of thiosulphates. The thiosulphate in the filtrate was estimated iodometrically, the solution being first acidified with acetic acid (Müller, *loc. cit.*). The mean of several results gave 61·86% of potassium recovered as potassium sulphate and 38·16% as potassium thiosulphate. The sum of these values, 100·02, shows that the whole of the potassium is eventually recovered in these two forms. Practically the same values were obtained from experiments at temperatures ranging from −3° to

+76°. The values approximate to three molecules of potassium sulphate to two of potassium thiosulphate, and the result, when the reaction is complete, can be summed up in the equation

$$10KMnO_4+22H_2S=3K_2SO_4+2K_2S_2O_3+10MnS+22H_2O+5S.$$

At the end of the reaction the solution is alkaline and, if it is not acidified before the titration with iodine, the values for the thiosulphate are always high. Control experiments showed that the lead carbonate used to remove the excess of hydrogen sulphide from the solution has no action on the thiosulphate. The thiosulphate found in a solution (4·170 g. per litre) which had been treated with hydrogen sulphide, shaken with lead carbonate, filtered, and then titrated against iodine was 4·164; 4·167; 4·170; and 4·165 g. per litre.

(2) *Investigation of the Mechanism of the Reaction by a Study of Two Intermediate Stages.*—Hydrogen sulphide was passed through the solution until the hydrated manganese dioxide was converted into a dirty yellow, granular mass. The values then found for potassium recovered as sulphate and as thiosulphate were 59·61, 58·54% and 34·32, 32·45%, respectively, of the total potassium. Since the sum of these values (93·93, 90·99) does not account for all the potassium present, it appears that some other sulphur compound of potassium is first formed which is subsequently decomposed by hydrogen sulphide into potassium sulphate and thiosulphate; the average final values for potassium recovered as sulphate and as thiosulphate were 61·66% and 38·27%, respectively (sum, 99·93). This compound may be one (or more) of the polythionates, for penta-, tetra-, and tri-thionates are known to be thus decomposed by hydrogen sulphide (Debus, J., 1888, **53**, 328) and the authors have shown that dithionates slowly undergo a similar change in presence of this gas.

Identification of the Compounds formed in Solution when the Manganese is precipitated as Hydrated Manganese Dioxide.

A solution of potassium permanganate was shaken with successive small quantities of half-saturated aqueous hydrogen sulphide until the brown colour just disappeared. (When this was done carefully with standard solutions, it was not possible to obtain a definite end-point.) The filtered liquid, which was faintly alkaline, contained sulphate, thiosulphate, and dithionate, but no sulphide, sulphite, penta-, tetra-, tri-thionate, colloidal sulphur or manganese. In view of the difficulty of testing for thionates in presence of one another, the tests given (p. 2) were performed both on the filtrate and on control solutions of thionates of known concentrations.

The distinction between thiosulphate, dithionate, and trithionate was made as follows : The solution decolorised iodine solution and gave a black precipitate with silver nitrate. (The solution gave no precipitate when warmed with hydrochloric acid. This was due to the low concentration of the thiosulphate.) Dilute aqueous potassium permanganate added to the solution was first bleached (thiosulphate), then a blood-red coloration developed, and brown hydrated manganese dioxide was slowly precipitated. This suggested the presence of tri- or di-thionate. The filtrate from the precipitation of the sulphate by barium chloride was warmed with dilute hydrochloric acid ; sulphur dioxide was detected, but sulphur was not deposited. Sulphate was detected in the solution (distinction from thiosulphate). Trithionates give sulphur dioxide, sulphate, and sulphur. Dithionates give sulphur dioxide and sulphate only. In dilute solutions the sulphur may not be precipitated. Mercuric chloride gives a yellow precipitate with trithionates, but does not react with dithionates. With this reagent, the filtrate gave a white turbidity. This is given by thiosulphates in very dilute solution. This suggests the absence of trithionates and the presence of thiosulphate. Ammoniacal silver nitrate had no action on the filtrate. A trithionate would have given a brown coloration.

Action of Hydrogen Sulphide on Hydrated Manganese Dioxide.

The blackish-brown precipitate of hydrated manganese dioxide obtained by the action of dilute aqueous sodium hypochlorite on a solution of manganous chloride, after being thoroughly washed with water, was free from alkali, chloride, and hypochlorite. It was suspended in water, through which scrubbed hydrogen sulphide was then bubbled for some time. A large proportion of the dioxide was converted into manganese sulphide contaminated with sulphur, and the solution, which was neutral to phenolphthalein, contained manganese as sulphate and thiosulphate. Ordinary dry A.R. manganese dioxide, when suspended in water and treated with hydrogen sulphide, gave the same results, and so also did hydrated manganese dioxide formed by the action of hydrogen sulphide on potassium permanganate and washed free from sulphate and thiosulphate and until the washings gave no indication of alkalinity with phenolphthalein. The presence of dithionate was not definitely proved, but independent experiments showed that manganese dithionate is decomposed by hydrogen sulphide into the sulphate and thiosulphate.

If neutral potassium sulphate was added to the water in which the hydrated manganese dioxide was suspended, the solution, in which manganese could not be detected, became alkaline to phenol-

phthalein and, when hydrogen sulphide was passed into it, the manganese was completely converted into manganous sulphide. The alkalinity was probably due to the adsorption of sulphate ions of the potassium sulphate. This would also account for the alkalinity of the solution in the reaction under investigation.

Quantitative Estimation of Intermediate Products in the Filtrate.

A dilute solution of potassium permanganate was treated with half-saturated aqueous hydrogen sulphide in the way described on p. 3, the precipitate was well washed, and the washings and the filtrate were made up to a definite volume. Care was taken that the solution contained no free hydrogen sulphide. In aliquot portions, the sulphate and thiosulphate were estimated as described on p. 2, and the dithionate by Szentpaly-Peyfuss's method (*Z. anorg. Chem.*, 1924, **131**, 203).

TABLE I.

Estimation of Sulphate, Thiosulphate, and Dithionate in the Filtrate.

Percentage of the potassium recovered as sulphate	thiosulphate	dithionate.	Total recovered.
69·70 (79·72)	4·84 (19·98)	25·06	99·60
79·87 (83·67)	10·27 (15·98)	9·51	99·65
68·08 (78·82)	4·65 (20·76)	26·84	99·57

The potassium is quantitatively accounted for as sulphate, thiosulphate, and dithionate, but the results show variations in the proportions in which the components are present. If it is assumed that the dithionate decomposes quantitatively into sulphate and thiosulphate, the values given in brackets would be obtained for potassium as sulphate and thiosulphate.

The results can be reconciled with the average values of 61·66 and 38·27% found for the potassium recovered as sulphate and thiosulphate, respectively, in the completed reaction (p. 3) as follows. When a large excess of hydrogen sulphide is passed, air is practically excluded from the reaction. Possibly, also, any oxidising action of the hydrated manganese dioxide is confined to the hydrogen sulphide, because dithionates are not oxidised by manganese dioxide. It is suggested, therefore, that the first products of the reaction are potassium sulphate, potassium dithionate, hydrated manganese dioxide, and sulphur; all attempts to stop the action at this stage, however, have failed. The stoicheiometric proportions in which the potassium sulphate and thiosulphate are found at the end of the reaction preclude the possibility of potassium dithionate being the only potassium salt first formed. The

second stage of the action may be represented by the equations

$$5K_2S_2O_6+13H_2S=3K_2S_2O_3+2K_2SO_4+13H_2O+15S \quad . \quad . \quad . \quad (1)$$

$$xMnO_2,yMnO,zH_2O+(2x+y)H_2S=(x+y)MnS+(2x+y+z)H_2O+xS,$$

and hence the final result is potassium sulphate and thiosulphate in solution and a precipitate of manganous sulphide and sulphur. When the dilute solution is shaken with hydrogen sulphide, air dissolves freely and a part of the dithionate is directly oxidised to sulphate at the expense of the thiosulphate which would otherwise have been formed from the dithionate in the presence of excess of hydrogen sulphide. Excess of hydrogen sulphide thus does the double duty of reducing the dithionate to sulphate and thiosulphate and protecting it from oxidation by dissolved air. In support of this argument, attention is directed to the results on p. 3. These represent a stage intermediate between those for the final values (K_2SO_4, 61·66%; $K_2S_2O_3$, 38·27%) and those given in Table I, *i.e.*, a stage in which the "protecting" action of the hydrogen sulphide has been fully exerted but in which its reducing action has been stopped before completing its work. Assuming the decomposition of the dithionate into sulphate and thiosulphate in the sense of equation (1), the values on p. 3, calculated for the final product, become $59·61 + (0·4 \times 6·07) = 62·04$ and $58·54 + (0·4 \times 9·01) = 62·14$ for the percentage of potassium present in solution as sulphate and $34·32 + (0·6 \times 6·07) = 37·96$ and $32·45 + (0·6 \times 9·01) = 37·86$ for the percentage of potassium present as thiosulphate.

These results support the argument that the hydrogen sulphide has a protecting and reducing action, since, in the completed reaction, it was used in excess of that required for the first stage and air could have taken little or no part in the reaction.

Summary.

The first products of the reaction between hydrogen sulphide and potassium permanganate in dilute solution appear to be colloidal hydrated manganese dioxide, which quickly coagulates to a gelatinous precipitate; sulphur; and potassium sulphate and potassium dithionate in solution.

When excess of hydrogen sulphide is passed through the solution, the hydrated manganese dioxide is converted into manganous sulphide with the separation of sulphur. The manganous sulphide is first formed as a colloid, which quickly coagulates to pink manganous sulphide. Excess of hydrogen sulphide decomposes the potassium dithionate into potassium sulphate and thiosulphate with the simultaneous formation of sulphur. A portion of the

sulphur is precipitated; the rest is in colloidal solution and is completely precipitated on standing.

The solution is alkaline throughout. This is probably due to the adsorption of the anions of the potassium salts by the hydrated manganese dioxide or manganous sulphide.

GOVERNMENT COLLEGE, LAHORE, PUNJAB,
INDIA. [*Received, June 26th,* 1925.]

II.—*Preparation of 1-Halogeno-2-nitronaphthalenes and 2-Nitronaphthalene.*

By HERBERT HENRY HODGSON and ERNEST KILNER.

2-NITRO-1-NAPHTHYLAMINE is readily obtained from 2-nitro-1-naphthol, which is itself best prepared by the oxidation of 2-nitroso-1-naphthol (Hodgson and Kilner, J., 1924, **125**, 807). For the preparation of large quantities of 4-nitro-1-naphthylamine Morgan and Micklethwait's modification (J., 1905, **87**, 928) of Lellmann and Remy's method is serviceable.

Hydrolysis of aceto-1-nitro-β-naphthalide proceeds better with acid than with alcoholic potassium hydroxide (Liebermann and Jacobson, *Annalen*, 1882, **211**, 44), which produces a substantial quantity of 1-nitro-2-naphthol.

By very slow decomposition in the cold in presence of cuprous chloride and concentrated hydrochloric acid, diazotised 2-nitro-1-naphthylamine gives a good yield of 1-*chloro*-2-*nitronaphthalene*. Under similar conditions, only poor yields of the corresponding *bromo*- and *iodo*-compounds are obtained, which may be due to the preferential formation of naphthalene-1-diazo-2-oxide (compare Friedländer, *Ber*, 1895, **28**, 1951; Morgan and Evens, J., 1919, **115**, 1126). Vesely's electrolytic method (*Ber.*, 1905, **38**, 136) proved unsuitable for the preparation of 1-chloro-2-nitronaphthalene.

These substances all have an extremely irritating action on the skin.

EXPERIMENTAL.

2-*Nitro*-1-*naphthylamine*.—A finely powdered mixture of 2-nitro-1-naphthol (5 g.) and ammonium carbonate (3 g.) is made into a paste with concentrated ammonia (10 c.c.) and water (6 c.c.), and heated in a sealed tube at 120—130° for 6 hours. The product when cold is pulverised, and boiled with 200 c.c. of water, aqueous ammonia being occasionally added. The solution, containing the ammonium salt of unchanged 2-nitro-1-naphthol (0·31 g.), is filtered and the solid is dried and extracted with boiling alcohol (150 c.c.).

The extract on evaporation leaves 2-nitro-1-naphthylamine (3·8 g.), which melts at 141°, and at 144° after recrystallisation from alcohol (Lellmann and Remy, *Ber.*, 1886, **19**, 797; 1887, **20**, 872, give m. p. 144°). The substance insoluble in alcohol (about 0·52 g.) does not melt at a high temperature and is probably 2 : 2′-dinitrodinaphthylamine (Found: N, 12·0. $C_{20}H_{13}O_4N_3$ requires N, 11·7%). An experiment made in an autoclave produced 16 g. of 2-nitro-1-naphthylamine and 1·3 g. of insoluble material from 20 g. of 2-nitro-1-naphthol, 1·8 g. of which were recovered.

4-*Nitro*-1-*naphthylamine*.—Experiments similar to the above carried out with 4-nitro-1-naphthol indicated an optimum reaction temperature between 140° and 160°. The quantities of 4-nitro-1-naphthylamine, material insoluble in alcohol, and recovered 4-nitro-1-naphthol, respectively, were: (at 120—130°) 0·5 g., ——, and 6·8 g. from 8 g.; (at 140°) 2·82 g., 0·24 g., and 1·73 g. from 5 g.; (at 160—165°) 2·94 g., 1·43 g., and 0·2 g. from 5 g. of 4-nitro-1-naphthol. The nitronaphthylamine obtained at 140° melted at 182°, and at 191° after crystallising once from alcohol.

1-*Nitro*-2-*naphthylamine*.—A mixture of β-naphthylamine * (1 part), 50% acetic acid (5 parts), and acetic anhydride (1 part) is boiled under reflux for 1 hour; on cooling, aceto-β-naphthalide separates in flaky crystals. This product (200 g.) is added in four equal portions to cold glacial acetic acid (250 c.c.), into which, after each of the first three additions, 70% nitric acid (15 c.c.) is run during 1 hour, the temperature being kept at 8—10°. This procedure obviates the stiffening of the reaction mixture which renders Liebermann and Jacobson's process (*loc. cit.*) almost unworkable. After the last addition of aceto-β-naphthalide, 25 c.c. of nitric acid are added to the mixture, which is then kept for 2 days. The orange-yellow aceto-1-nitro-β-naphthalide that has separated is filtered off and washed with ether (yield 170 g.).

Hydrolysis is effected by boiling a solution of the product (125 g.) in alcohol (500 c.c.) with concentrated hydrochloric acid (125 c.c.) for 4 hours; the treatment is repeated if necessary. The mixture is then poured into 4 litres of cold water and the crude 1-nitro-2-naphthylamine filtered off, dried, and recrystallised from twice its weight of hot alcohol; m. p. 122° (Atterberg gives m. p. 124—125°, and Meldola, 126—127°) (Found: N, 15·0. Calc., 14·9%).

1-*Chloro*-2-*nitronaphthalene*.—Five grams of sieved 2-nitro-1-naphthylamine are warmed with 30 c.c. of a mixture of 98% sulphuric acid (3 vols.) and water (1 vol.) (*i.e.*, H_2SO_4,H_2O). The solution thus obtained is cooled to 0°, stirred, and solid sodium

* Pinnow's directions (*Ber.*, 1900, **33**, 417) for acetylating α-naphthylamine give an unsatisfactory result in the case of β-naphthylamine.

nitrite (3—4 g.) gradually added, the temperature being kept below 5°. The diazo-solution is added carefully to a cooled solution of cuprous chloride (5 g.) in concentrated hydrochloric acid (40 c.c.). After 12 hours, the solid is filtered off, dried, and extracted with hot alcohol (50 c.c.). The extract is poured into 1% aqueous sodium hydroxide (100 c.c.), which dissolves any 2-nitro-1-naphthol present. The precipitate is filtered off, washed, and distilled with superheated steam. The solid (2·5 g.) in the distillate, after two crystallisations from alcohol, forms long, pale yellow needles, m. p. 76° (Found: N, 7·1; Cl, 16·7. $C_{10}H_6O_2NCl$ requires N, 6·7; Cl, 17·1%). 1-Chloro-2-nitronaphthalene does not depress the melting point of 2-nitro-1-naphthol.

1-*Bromo*-2-*nitronaphthalene*.—The above procedure was repeated, except that the Sandmeyer reaction was carried out in a cooled mixture of crystallised copper sulphate (5·4 g.), copper bronze (1·4 g.), sodium bromide (15 g.), and water (40 g.). The solid obtained (0·95 g.) crystallised from alcohol in stout, bright yellow needles, m. p. 97° (Found: N, 5·8; Br, 31·5. $C_{10}H_6O_2NBr$ requires N, 5·55; Br, 31·7%).

1-*Iodo*-2-*nitronaphthalene*.—The Sandmeyer reagent in this case was potassium iodide (6 g.) in water (50 c.c.). The solid product was treated with sodium bisulphite solution to remove iodine, and crystallised from alcohol in pale yellow plates, m. p. 111° (yield 1·9 g.) (Found: I, 42·7. $C_{10}H_6O_2NI$ requires I, 42·4%).

2-*Chloro*-1-*nitronaphthalene*.—1-Nitro-2-naphthylamine (5 g.) was diazotised according to Friedländer and Littner (*Ber.*, 1915, **48**, 330), and from the resulting solution 1 g. of 2-chloro-1-nitronaphthalene was obtained.

2-*Nitronaphthalene*.—A mixture of 2-nitro-1-naphthylamine (4·2 g.), alcohol (12 c.c.), and concentrated sulphuric acid (3 c.c.) was cooled to 0°, 3·4 c.c. of aqueous sodium nitrite (50 g. in 100 c.c. of solution) were added during 30 minutes, and the whole was kept in the cold for 4 hours. It was then gradually heated to the boiling point during 5 hours, boiled for 2 hours, poured into cold water (300 c.c.), 20% aqueous sodium hydroxide (20 c.c.) was added, and the mixture was steam-distilled. The pure 2-nitronaphthalene in the distillate solidified in yellow crystals (1·24 g.) with a cinnamon-like odour, m. p. 79° (Found: N, 8·2. Calc., N, 8·1%).

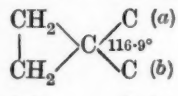
The authors desire to thank the British Dyestuffs Corporation for gifts of chemicals used in this investigation.

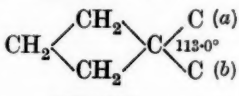
TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, July 25th*, 1925.]

III.—*The Influence of Carbon Rings on the Velocity of Reactions involving their Side Chains. Part I. The Hydrolysis of Cyclic and Open-chain Malonic Esters.*

By RICHARD GANE and CHRISTOPHER KELK INGOLD.

IT has been shown during the last 10 years that the angle between two of the valencies of a carbon atom may be materially affected by structural conditions relating to the other two valencies, such as, for instance, their inclusion in a ring (Beesley, Ingold, and Thorpe, J., 1915, **107**, 1080, and later papers) or their attachment to groups of larger or smaller molecular volume (Ingold, J., 1921, **119**, 305, and later). Thus, on passing through the series (I) to (IV) an increasing

(I.) 



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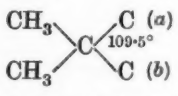
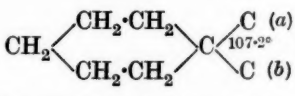
(III.) 

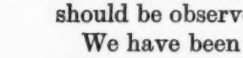


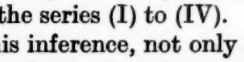
(IV.)

tendency towards the interaction of groups attached to carbon atoms (*a*) and (*b*) proves that these two carbon atoms are brought together by the widening of the angle between the remaining two valencies of the central carbon atom.

The opposite sequence would be expected if we were to examine, not the *inter*action of groups attached to carbon atoms (*a*) and (*b*), but their *independent* action on some external reagent. Evidently the proximity of the carbon atoms would now be, not an accelerating, but a retarding influence, and a *decreasing* tendency to reaction should be observed on passing through the series (I) to (IV).

We have been induced to examine this inference, not only for its own interest, but also because the large choice of replacement and addition reactions available renders it possible to select reactions capable of more exact study than the violent ring-forming processes employed in the investigations referred to above. This paper contains a record of experiments on the relative rates of hydrolysis by alkalis of a series of cyclic malonic esters of type (V), certain open-chain malonic esters (type VI) being included for comparison.

(V.) 



(VI.)

The remarkable effect of different carbon rings in promoting or retarding reactions in which only their side-chains and not the rings themselves are involved was first impressed on us when comparing

the experiences of Fischer and Dilthey (*Ber.*, 1902, **35**, 844) with those of Ingold, Sako, and Thorpe (J., 1922, **121**, 1177) when studying the formation of amides from malonic esters by the aid of aqueous ammonia. This case appears to have special analogies with results recorded in this paper, and must briefly be considered.

The most rational view of amide formation from esters appears to be that it is the result of two consecutive reversible addition reactions, the first of the aldehyde–ammonia, and the second of the ketone–alcoholate (semi-acetal) type :

$$-C(OEt){:}O + NH_3 \rightleftharpoons -C(OEt)(OH)\cdot NH_2 \rightleftharpoons -C({:}O)\cdot NH_2 + EtOH.$$

Fischer and Dilthey, however, were influenced by the fact that, whilst ethyl malonate and ethyl methylmalonate (VII and VIII) readily yield amides with aqueous ammonia, ethyl dimethylmalonate (IX) refuses to do so, and they therefore formulated the reaction, not as a direct attack by ammonia upon the carbethoxyl groups, but as a complex process involving a tautomeric hydrogen atom (*), the presence of which in (VII) and (VIII) enables a salt of type (X) to be formed as an intermediate product.

(VII.) $H\overset{*}{H}C<^{CO_2Et}_{CO_2Et}$ $\quad$ $(CH_3)\overset{*}{H}C<^{CO_2Et}_{CO_2Et}$ (VIII.)

(IX.) $(CH_3)_2C<^{CO_2Et}_{CO_2Et}$ $\quad$ $-C<^{CO_2Et}_{C(ONH_4)OEt}$ (X.)

Ingold, Sako, and Thorpe (*loc. cit.*), and at about the same time Dox and Yoder independently (*J. Amer. Chem. Soc.*, 1921, **43**, 2097), prepared without difficulty amides from the cyclic malonic esters (XI) and (XII) which, however, are devoid of a malonyl hydrogen atom.

$CH_2>C<^{CO_2Et}_{CO_2Et}$ (XI.) $\quad$ $CH_2<^{CH_2}_{CH_2}>C<^{CO_2Et}_{CO_2Et}$ (XII.) $\quad$ $CH_2<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>C<^{CO_2Et}_{CO_2Et}$ (XIII.)

These observations appear to some extent to rehabilitate the reversible addition mechanism, and to suggest a spatial explanation of the differences noticed. When it is reflected also that amide-formation occurred more easily with the *cyclo*propane than with the *cyclo*butane ester, it seems clear that at least a part of the observed differences is to be accounted for on stereochemical grounds. The special mechanism suggested by Fischer and Dilthey cannot be positively excluded from participation in the cases to which it applies; it must, however, be regarded, not as the general mechanism of amide formation, but only as a possible auxiliary process by means of which amide formation may be facilitated when enolisation of the ester can occur.

Bearing these points in mind, we have examined the velocity of hydrolysis not only of cyclic and disubstituted malonic esters such as (IX), (XI), (XII), and (XIII), but also of a series of malonic esters

FIG. 1.

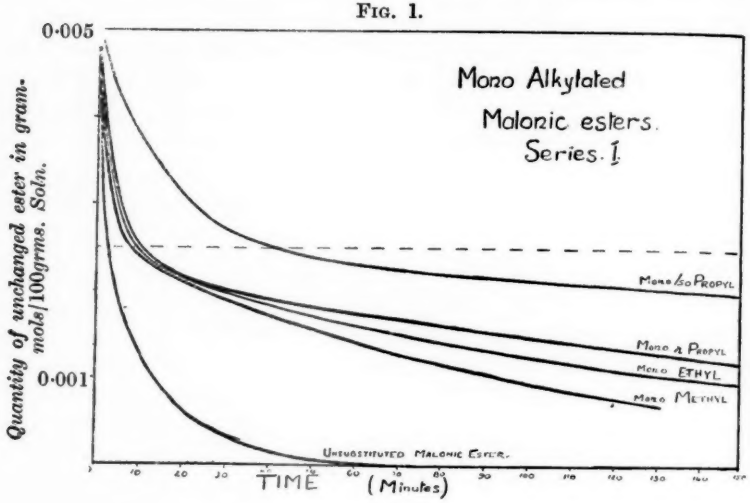
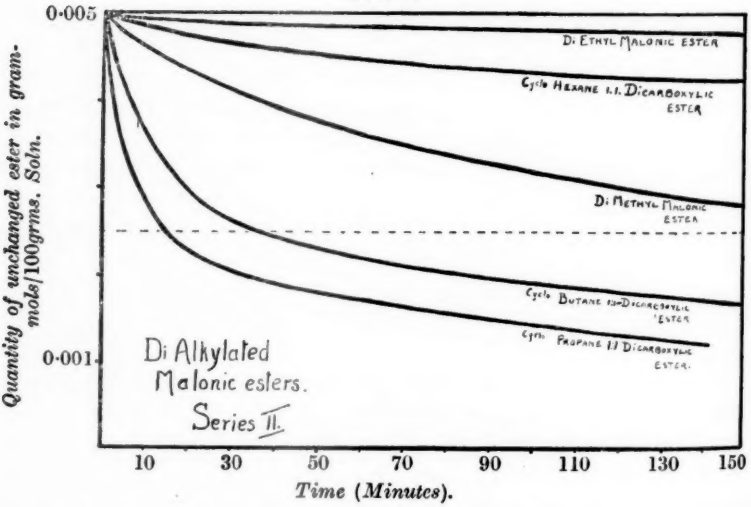


FIG. 2.



possessing a mobile hydrogen atom. The results of some of these determinations, carried out under strictly comparable conditions, are displayed in Figs. 1 and 2.

Attempts to calculate coefficients and construct such curves

theoretically led to considerable mathematical difficulties, principally owing to the distortion which experimental errors underwent in the process of evaluating coefficients. In its simplest aspect, and neglecting all corrections, the complete hydrolysis must be regarded as a pair of consecutive bimolecular reactions, but calculating on this basis it was found that effects of an arbitrary variation of one of the determined coefficients could often be largely counterbalanced by adjusting the other. Finally an approximate numerical comparison of the different cases was obtained by calculating the initial velocities from a series of curves representing identical conditions of temperature and initial concentration.

These initial velocities, $\dot{x}_0$, which were calculated from the following equations,

$$\dot{x} = K(a - x)(b - x); \; K_0 = \lim_{x \to 0} K; \text{ and } \dot{x}_0 = K_0 ab,$$

are exhibited for the disubstituted malonic esters (cyclic and open-chain) in the following table, the last column of which displays the angle between the valencies carrying the carboxyl groups calculated according to the principles advanced by Beesley, Ingold, and Thorpe (*loc. cit.*).

TABLE I.

	$\dot{x}_0 \times 10^4$.	$\log_{10} \dot{x}_0$.	θ.
*cyclo*Propane-1 : 1-dicarboxylic ester	4·95	$\bar{4}$·69	116·9°
*cyclo*Butane-1 : 1-dicarboxylic ester	2·3 (5)	$\bar{4}$·37	113·0
gem-Dimethylmalonic ester	0·45	$\bar{5}$·65	109·5
*cyclo*Hexane-1 : 1-dicarboxylic ester	0·10	$\bar{5}$·00	107·2
gem-Diethylmalonic ester	0·02 (5)	$\bar{6}$·40	(105·3)

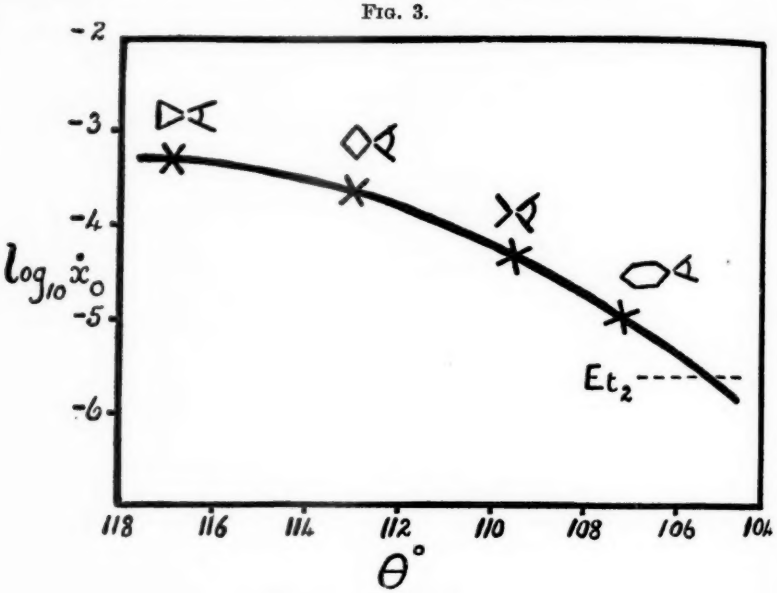
Reference to Fig. 3 shows that the points connecting the logarithms of the initial velocities and the calculated angles lie on a smooth curve both for the cyclic esters and the *gem*-dimethyl ester. There is no means at present of calculating the angle appropriate to the *gem*-diethyl ester, but the curve indicates a value of 105·3°, which is lower than might be expected from previous investigations with glutaric acids.

It was not found possible to deduce initial velocities in the cases of the tautomeric malonic esters represented in Fig. 1, as the reactions of these substances (excepting *iso*propylmalonic ester) were too rapid at their commencement for accurate measurement. The curves show, however, that the various alkyl groups exert an influence appropriate to their relative size, although it is difficult to express this effect quantitatively.

The fact that the reactions of this group proceed with much greater rapidity than the steric theory would indicate seems to show the operation of an additional mechanism when tautomeric hydrogen is present. Such a supposition would be consistent with that

discussed in the case of amide formation, with racemisation by alkalis of compounds containing potentially mobile hydrogen attached to asymmetric carbon, with the interconversion of sugars by alkalis, and numerous other well-known phenomena.

FIG. 3.



EXPERIMENTAL.

Preparation of Material.—(1) *Ethyl malonate.* A sample of Boots's pure ethyl malonate was carefully fractionated, head and tail fractions being rejected, and the main portion, which boiled well within 1°, being used.

(2) *Ethyl methylmalonate.* To avoid possible contamination of the monomethylation product of ethyl malonate with traces of the latter and of ethyl dimethylmalonate, the crude ester was hydrolysed and the acid crystallised several times from ether and water, and, after washing with hot chloroform, from ethyl acetate. The fully purified acid (m. p. 130°; recorded m. p. 129°) was then re-esterified by Fischer and Speier's method. The ester had b. p. 196—197°/754 mm.

(3) *Ethyl dimethylmalonate.* The crude dimethylation product of malonic ester was distilled (b. p. 193—195°) and, in view of possible contamination with incompletely methylated products, digested with an equal weight of ammonia (*d* 0·880), which rapidly converts the latter into amides. The pure dimethyl ester had b. p. 194—194·3°/751 mm. and b. p. 196—197°/765 mm.

(4) *Ethyl ethylmalonate.* Like (2).

(5) *Ethyl diethylmalonate.* Boots's sample of this ester was shaken with cold 30% sodium hydroxide sufficiently to hydrolyse any ethyl monoethylmalonate, recovered, and distilled (Michael, *J. pr. Chem.*, 1905, **72**, 537).

(6) *Ethyl* n-*propylmalonate.* The ester prepared as described by Conrad (*Annalen*, 1880, **204**, 124) was purified by distillation until it boiled within 1°.

(7) *Ethyl* iso*propylmalonate.* Like (6) (compare Preiswerck, *Helv. Chim. Acta*, 1923, **6**, 192).

(8) *Ethyl* cyclo*propane*-1 : 1-*dicarboxylate* (XI) was prepared and purified as described by Perkin (J., 1885, **47**, 810). B. p. 210—211°/718·5 mm.

(9) *Ethyl* cyclo*butane*-1 : 1-*dicarboxylate* (XII), prepared as described by Perkin (J., 1887, **51**, 2) and purified by repeated fractional distillations, had b. p. 224·5—225·5°/757·7 mm.

(10) *Ethyl* cyclo*hexane*-1 : 1-*dicarboxylate* (XIII). The specimen used was kindly given by Mr. W. A. Wightman. It had been subjected to partial hydrolysis, which would have removed any monosubstituted malonic ester if present [see (5)].

Method of Experiment.—The hydrolyses were carried out by means of carbonate-free aqueous-alcoholic sodium hydroxide contained in strong bottles, into which thin glass tubes containing the weighed ester (usually 0·005 g.-mol.) were dropped to start the reaction, the alkali having previously attained the thermostat temperature. The portions withdrawn for analysis were run as rapidly as possible into an excess of hydrochloric acid to terminate the reaction and titrated with $N/50$—$N/60$-barium hydroxide. Various temperatures and concentrations of alkali were employed, but in the experiments selected for this record the temperature was uniformly 27·0°, whilst the alkali consisted of 0·8380 g. of sodium hydroxide, 23·26 g. of water and 75·90 g. of alcohol in each case.

Results.—The general method of calculating the limiting velocities has been described above, and an instance may here be given of its application. In the following table, the figures of the first row are read from the slope of the smoothed x–t curve, and those in the bottom row show the asymptotic approach of k to the value $k_0 = 0{\cdot}0000090$; whence $\dot{x}_0 = 0{\cdot}00049$ can be calculated.

TABLE II.

(Ethyl *cyclo*propane-1 : 1-dicarboxylate.)

$\dot{x} \times 10^4$ ...	4·45	3·55	2·95	2·40	1·70	1·30	0·78
$x \times 10^4$ ...	2·25	6·20	9·50	1·21	1·62	1·92	2·24
$k \times 10^4$ ...	9·2	9·1	9·5	9·6	10·4	12·4	17·4 (rapidly increasing)

TABLE III.

(Mobile Esters.)

Ethyl malonate.		Ethyl methylmalonate.		Ethyl ethylmalonate.	
t (mins.).	$x \times 10^4$ (g.-mols.).	t (mins.).	$x \times 10^4$ (g.-mols.).	t (mins.).	$x \times 10^4$ (g.-mols.).
0·50	16·2	0·75	8·5	1·00	6·3
1·50	22·5	3·00	17·8	2·00	11·1
2·50	27·4	4·00	20·7	3·25	15·3
3·75	29·6	6·00	23·1	6·00	20·8
5·75	32·7	8·50	24·9	8·25	24·0
6·75	34·1	11·00	26·2	10·75	25·7
9·75	37·3	15·25	27·4	14·25	26·9
12·00	39·2	20·00	28·5	21·00	28·1
14·75	40·9	25·00	30·0	33·00	30·1
19·50	43·3	30·00	31·1	41·75	31·4
26·50	45·8	35·50	32·3	54·00	32·8
35·50	47·3	46·30	34·3	71·25	34·6
46·00	48·8	60·50	36·5	89·00	35·9
59·00	49·6	75·25	38·1	104·00	37·4
75·0	49·9	89·00	39·3	127·00	39·0
		100·00	40·7	144·00	39·9
		117·00	41·8	165·00	41·2
		131·00	43·0	194·00	42·2

Ethyl *n*-propylmalonate.				Ethyl *iso*propylmalonate.			
t (mins.).	$x \times 10^4$ (g.-mols.).	t (mins.).	$x \times 10^4$ (g.-mols.).	t (mins.).	$x \times 10^4$ (g.-mols.).	t (mins.).	$x \times 10^4$ (g.-mols.).
0·50	5·7	28·50	33·3	0·50	2·3	41·00	24·7
1·44	10·6	38·75	34·0	2·25	5·8	57·50	26·7
2·50	14·6	70·50	34·7	4·25	7·8	75·25	27·7
4·33	16·4	105·50	36·8	8·50	11·1	91·75	28·5
6·67	22·3	132·50	38·7	14·25	16·0	113·50	28·9
9·44	24·7	153·00	39·4	19·25	18·7	134·50	29·6
12·50	26·6	187·50	40·8	25·00	21·6	174·75	30·4
15·84	29·8	210·25	41·6	35·25	23·8		
20·00	31·2						

TABLE IV.

(Static Esters—Open-chain.)

Ethyl dimethylmalonate (" A ").				Ethyl dimethylmalonate (" B ").				Ethyl diethyl-malonate.	
t (mins.).	$x \times 10^4$ (g.-mols.).	t (mins.).	$x \times 10^4$ (g.-mols.).	t (mins.).	$x \times 10^4$ (g.-mols.).	t (mins.).	$x \times 10^4$ (g.-mols.).	t (mins.).	$x \times 10^4$ (g.-mols.).
0·75	0·3	84·50	16·4	1·50	0·7	85·00	16·9	1·50	0
1·50	0·6	102·25	17·9	3·75	1·3	102·75	17·8	13·00	0·3
3·00	1·3	116·50	19·2	6·25	2·1	121·50	19·3	22·50	0·6
6·84	2·4	138·00	20·6	10·00	3·4	148·50	21·2	34·50	0·9
14·84	4·9	158·75	22·1	17·00	5·6	174·67	22·4	48·25	1·1
26·00	7·4	183·75	23·1	25·75	7·5	201·00	23·5	110·00	1·5
36·75	9·8	200·50	23·8	33·50	8·5	223·00	23·9	181·00	2·2
46·50	11·3	212·25	23·9	41·75	10·6	244·00	24·8	218·00	2·4
56·84	12·9	229·50	24·6	52·75	11·7	278·50	25·0		
70·50	14·8	238·75	24·9	68·25	14·5	309·75	26·5		
				81·75	16·5				

TABLE V.

(Static Esters—Cyclic.)

Ethyl *cyclo*propanedicarboxylate.				Ethyl *cyclo*butanedicarboxylate.				Ethyl *cyclo*hexanedicarboxylate.	
t (mins.).	$x \times 10^4$ (g.-mols.).	t (mins.).	$x \times 10^4$ (g.-mols.).	t (mins.).	$x \times 10^4$ (g.-mols.).	t (mins.).	$x \times 10^4$ (g.-mols.).	t (mins.).	$x \times 10^4$ (g.-mols.).
0·50	2·8	29·50	29·5	0·50	1·0	44·00	26·3	3·75	0·5
1·75	6·9	34·25	29·9	1·75	3·3	51·00	27·4	7·00	0·8
2·75	10·4	39·00	30·4	3·75	7·2	62·75	28·3	14·00	1·5
4·00	13·1	47·75	31·4	6·50	10·9	78·50	29·8	29·50	2·8
5·50	17·3	56·00	32·6	9·00	13·5	103·50	31·6	49·50	3·9
8·25	19·9	68·50	33·7	14·00	17·0	128·50	32·8	61·00	4·8
11·50	22·6	84·50	35·1	19·33	19·5	147·75	33·2		
14·00	24·6	96·00	35·5	25·33	21·6	170·00	34·4		
17·00	25·7	113·50	36·5	30·00	23·8	188·25	34·9		
20·25	26·9	134·25	37·8	35·20	24·6	207·00	36·1		
24·00	28·3	160·75	38·2						

We desire to thank the Chemical Society for a grant which has covered much of the cost of this investigation.

THE UNIVERSITY, LEEDS. [*Received, November 18th*, 1925.]

IV.—*Tesla-luminescence Spectra. Part VI. Some Amino-derivatives.*

By WILLIAM HAMILTON MCVICKER, JOSEPH KENNETH MARSH, and ALFRED WALTER STEWART.

IN previous papers (J., 1923, **123**, 642, 817, 2147; 1924, **125**, 1743; 1925, **127**, 999) accounts were given of the Tesla-luminescence spectra of various benzene derivatives. The present communication contains a description of the emission spectra of some aromatic amino-derivatives. The apparatus used is the same as before, the pressures were 1—2 mm., and the exposure was in each case 15 minutes.

Aniline, b. p. 182·9°/748 mm. A strong continuous spectrum, 2880—4000 Å.U., fading off gradually at both ends, with a number of well-defined narrow bands at 2895, 2915, 2927, 2938, 2960, 2976, 2985, 2999, 3010, 3022, 3031, 3050, 3070, 3098, 3122, 3145, 3171, 3199, 3224.

The spectra of the next seven substances faded gradually at both ends, but more so at the end of greater wave-length.

Monomethylaniline, b. p. 196·4—196·9°/770 mm. A strong continuous spectrum at approximately 2965—4250 Å.U. The centre of maximum intensity is about 3300 Å.U.

Monoethylaniline, b. p. 205·6—206·2°/770 mm. A strong continuous spectrum at approximately 2695—4250 Å.U. The centre of maximum intensity is about 3340 Å.U.

Dimethylaniline, b. p. 194·2—194·3°/766 mm. A strong continuous spectrum at approximately 3025—4300 Å.U. Centre of maximum intensity at approximately 3420 Å.U.

Diethylaniline, b. p. 213·2—214°/738 mm. Medium continuous spectrum at approximately 3010—4225 Å.U. Centre of maximum intensity at approximately 3375 Å.U.

iso*Amylaniline*, b. p. 253·6—255·6°/766 mm. Strong continuous spectrum at approximately 2995—4300 Å.U. Centre of maximum intensity at about 3340 Å.U.

Benzylamine, b. p. 184·6—185·2°/771 mm. Weak continuous spectrum at approximately 2671—3390 Å.U. Diffuse heads of bands at 2671, 2714, 2800.

Benzylaniline, b. p. 320·8—321·0°/775 mm. Strong continuous spectrum at approximately 2980—4225 Å.U. Centre of maximum intensity at approximately 3345 Å.U.

Diphenylamine, b. p. 302·6—302·8°/750 mm. Weak continuous spectrum at approximately 3070—3875 Å.U., fading off gradually at both ends.

Triphenylamine. Nine times recrystallised from alcohol and boiled once with animal charcoal. M. p. 126·4°. Moderate continuous spectrum at approximately 3260—4220 Å.U., fading off gradually at both ends.

Benzidine, m. p. 125—127°. Strong continuous spectrum at about 3200—4600 Å.U., fading off gradually at both ends but more so at the end of shorter wave-length. Centre of maximum emission at approximately 3830 Å.U.

Hydrazobenzene, m. p. 126—127°. Very faint, continuous spectrum at approximately 3050—4125 Å.U., fading off gradually at both ends, but more so at end of greater wave-length. Centre of maximum intensity at approximately 3340 Å.U.

Phenylhydrazine, b. p. 241·0—241·5°/763 mm. Weak continuous spectrum at approximately 2980—3640 Å.U., fading off gradually at both ends. Possibly there are faint narrow bands at 3024 and 3052 Å.U.

α-*Methylphenylhydrazine*, b. p. 101—103°/28—29 mm. Strong continuous spectrum at approximately 2940—4225 Å.U., fading off gradually at both ends, but more so at the end of greater wave-length. Centre of maximum intensity at approximately 3345 Å.U.

α-*Naphthylamine*, b. p. 299·4—299·7°/774 mm. Intense continuous spectrum at approximately 3320—4700 Å.U., fading off gradually at both ends with a diffuse head at about 3780 Å.U.

Signs of very indistinct bands were observed at approximately 3340, 3399, 3443, and 3506 Å.U., but the phenomena are doubtful.

β-*Naphthylamine*, m. p. 110°. Intense continuous spectrum at approximately 3280—4700 Å.U., fading off gradually at both ends. Centre of maximum intensity at approximately 3800 Å.U.

Ammonia. The ammonia spectrum contains two maxima at 3360 and 3371 Å.U. and a band system extending from these in both directions to 3286 and 3450, respectively. Possibly there may be two bands in the visible region at 5690 and 6600 Å.U. These bands are very indefinite. The spectrum in general is that of ammonia in a vacuum tube excited by an ordinary induction coil discharge.

On collating the foregoing data, some points of interest are found. The attachment of the amino-group directly to the benzene ring has the effect of shifting the region of emission towards the red end. Replacement of the hydrogen atoms of the amino-group by alkyl radicals has no profound influence on the spectral character of the emission. When phenyl groups are introduced into the amino-radical, the first phenyl group weakens the intensity of the spectrum as a whole, whilst a second phenyl radical increases the intensity slightly, though not enough to bring it back to the intensity of aniline.

The replacement of one hydrogen atom of the amino-group by the group $-NH_2$ so as to form phenylhydrazine, has a marked influence on the spectrum. Aniline has a strong emission with a length of 1120 units; the emission of phenylhydrazine is weak and extends over only 660 units. If the imino-group of phenylhydrazine carries a methyl group, $NMePh{\cdot}NH_2$, both the intensity and the extent of the emission are increased. On the other hand, the introduction of a phenyl group, forming NHPh·NHPh, weakens the intensity of the spectrum but increases the extent of the emission.

The influence of constitution upon the spectra is seen by comparing the following data:

		Intensity.	Emission region.
Diphenylmethane	CH_2Ph_2	Medium	2673—3900
Diphenylamine	$NHPh_2$	Weak	3070—3875
Dibenzyl	$CH_2Ph{\cdot}CH_2Ph$	Faint	2700—4300
Hydrazobenzene	NHPh·NHPh	Very faint	3050—4125
Benzidine	$NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$	Strong	3200—4600
Diphenyl	$C_6H_5{\cdot}C_6H_5$	Faint	2890—3900

Obviously when imino-groups are substituted for methylene groups the intensity is weakened and the spectrum is truncated at the violet end. Hydrazobenzene has a very faint spectrum, whereas the spectrum of benzidine is strong. The intensity of the benzidine spectrum is not due to the close proximity of the two

phenyl nuclei, since the parent substance, diphenyl, has only a faint spectrum. The difference in the spectra of the two isomeric compounds must therefore be sought in difference between the group —NH—NH— on the one hand and the two primary amino-groups on the other.

The introduction of an amino-group into naphthalene has the effect of shortening the original spectrum at both ends while making it more intense in the region in which it still persists.

We desire to express our indebtedness to the Research Fund Committee of the Society; and also to the Eastman Kodak Company, who supplied us with specially pure specimens of some of our materials.

THE SIR DONALD CURRIE LABORATORIES,
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NORTHERN IRELAND. [*Received, October 7th*, 1925.]

V.—*The Solubility of Sodium Iodide in Ethyl Alcohol.*

By FREDERICK ERNEST KING and JAMES RIDDICK PARTINGTON.

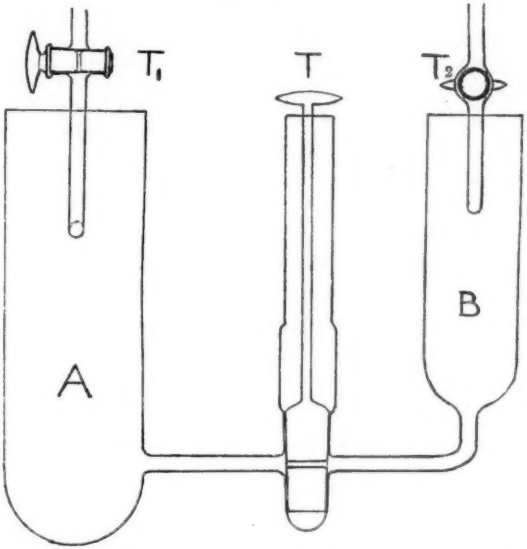
THE solubilities of the iodides of the alkali metals in alcohol require reinvestigation on account of the probable presence of moisture in the materials previously employed.

Preparation of the Materials.—Ethyl alcohol. Two litres of 96% alcohol were poured on to freshly burnt quicklime, refluxed for 6 hours, distilled, and refluxed over a further quantity of lime. The alcohol was distilled on to 5 g. of powdered silver nitrate previously dried at 110°, refluxed, and distilled. The distillate was refluxed with about 20 g. of fresh calcium turnings and distilled through a tall column, the first and last fractions of 100 c.c. being rejected. The alcohol was stored in a vessel with a siphon attachment and a guard tube of phosphorus pentoxide. The alcohol was free from aldehyde, ketone, ethyl nitrite, and ammonia. The density ($D_4^{25°}$) was 0·7851.

Sodium iodide. The iodide was prepared by decomposing pure sodium carbonate with hydriodic acid of constant b. p. (126°), prepared by the action of hydrogen sulphide on iodine in the presence of water. The solution of sodium iodide, slightly coloured with iodine from the decomposition of a little of the acid by the air, was evaporated to dryness and the solid recrystallised three times from water. The crystals of $NaI,2H_2O$ were heated in a large porcelain boat in a sloping glass tube through which a slow current of pure dry hydrogen was passing. The electrolytic hydrogen used in these

experiments was contained in a cylinder and was freed from oxygen by passing over heated platinised asbestos. As the water was driven off from the iodide the temperature was increased to 120°. The white solid was cooled in dry hydrogen, removed quickly, and ground up in a mortar contained in a desiccator over phosphorus pentoxide (Parker, J., 1914, **105**, 1504). Spectrum analysis failed to reveal the presence of other metals and the iodine content was shown to be 84·64% by precipitation as silver iodide (Theory, 84·66%).

FIG. 1.



Experimental.—On account of the hygroscopic nature of the solution the apparatus shown in Fig. 1 was devised. The apparatus was carefully dried and an excess of sodium iodide, together with the alcohol, placed in the tube A. The tube was closed with a good cork, which had been dried by heating in a wax-bath at 120°, and fitted with a glass stirrer. The air in the tube was displaced by dry hydrogen through the tap, T_1, and the vessel was then closed by pouring mercury into the seal surrounding the stirrer. Tube B was closed with a rubber bung, through which passed a filter tube packed with dry cotton wool, reaching to the bottom of B, with the top ground to take the end of a standard pipette. The capacity of A was approximately 80 c.c. and that of B 30 c.c. Tube B was filled with dry hydrogen and closed at the top of the filter tube with pressure tubing and a clip. Connexion between A and B could be made through the enclosed tap, T.

The apparatus was placed in a thermostat maintained at 25·0°, and the alcohol and iodide were stirred over-night. The stirring was then discontinued, and a sample of the saturated solution of iodide transferred to B through T by suction through T_2, dry hydrogen being admitted through T_1 to take the place of the solution removed. Quantities of approximately 10 c.c. of the solution were removed in standard pipettes and rapidly transferred to weighed evaporating flasks fitted with ground glass stoppers having two tubes sealed into them, the outer ends being provided with ground glass caps. The weights of the solutions were found, the solutions evaporated to dryness, the residues heated to 120° in a stream of dry hydrogen, and weighed. The solubility of sodium iodide in alcohol at 25° was found and an approximate value for the density of the solution as compared with water as a standard was calculated.

Results.—The figures under $S^{25°}$ represent the solubilities of sodium iodide in ethyl alcohol at 25° in g. per 100 g. of alcohol.

Expt. ...	1	2	3	4	5	6	7	8	9	10
$S^{25°}$	42·82	42·39	42·20	42·13	42·89	42·83	42·84	42·24	42·50	42·89

Density ($D_{4°}^{25°}$) = 1·037. Mean value of $S^{25°}$ = 42·57.

Pure dry lithium iodide has been prepared by heating the monohydrate in a current of dry nitrogen free from oxygen, and investigations on the influence of the solubility of lithium iodide on the solubility of sodium iodide in alcohol are in progress.

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON. [*Received, November 13th*, 1925.]

VI.—*The Structure of the Normal Monosaccharides. Part III. Rhamnose.*

BY EDMUND LANGLEY HIRST and ALEXANDER KILLEN MACBETH.

As earlier work led to the conclusion that normal derivatives of the pentose sugars xylose and arabinose have the amylene-oxidic structure (Hirst and Purves, J., 1923, **123**, 1352; Hirst and Robertson, J., 1925, **127**, 358), it was obviously of interest to determine the structure of normal derivatives of a typical methyl pentose. Evidence is now submitted showing that *l*-rhamnose and its stable derivatives also are amylene-oxidic. This view conflicts with the suggestion of Pringsheim ("Zuckerchemie," 1925, p. 102) that a butylene-oxidic structure for rhamnose follows from the apparently definite furoidal structure of rhamnal (Bergmann and Schotte, *Ber.*, 1921, **54**, 404). Fischer, Bergmann, and Rabe (*Ber.*, 1920, **53**, 2362) found, however, that during the conversion of aceto-

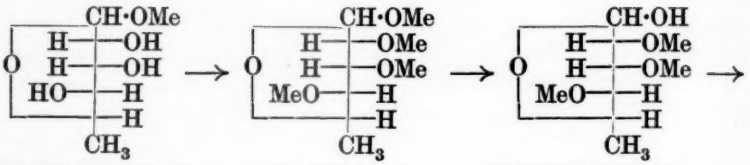
bromorhamnose into triacetyl methylrhamnoside a mixture of isomeric substances is formed by the wandering of acetyl groups accompanied by corresponding changes in the nature of the oxidic linkings. We are therefore of the opinion that it would be unsafe to base the structure of rhamnose derivatives on that of rhamnal, and, when considered in the light of the work now described, the presence of a γ-oxidic linking in triacetyl rhamnal is to be taken rather as evidence of the occurrence of an isomeric change during the reduction of acetobromorhamnose than as proof of the constitution of rhamnose itself.

The observations of Fischer, Bergmann, and Rabe led us to consider with special care the stability of the methoxyl groups in methylated rhamnose, for any wandering of the methyl groups would complicate very seriously the oxidation method we proposed to use in determining the structure of the compound. A wandering of a methyl group from position 6 to position 3 in the glucose molecule has been suggested (Ohle, *Ber.*, 1924, **57**, 403) to explain certain discordant observations in the chemistry of the acetone derivatives of the sugars, but, so far as we are aware, no case of such a transformation has been encountered during the oxidation of a methylated carbohydrate. Both γ- and normal derivatives oxidise to stable methoxy-acids without wandering of the methyl groups (compare, *e.g.*, Irvine, Fyfe, and Hogg, J., 1915, **107**, 539; Irvine and Oldham, J., 1921, **119**, 1744; Pryde, J., 1923, **123**, 1808; Levene, *J. Biol. Chem.*, 1924, **60**, 167; Haworth and Baker, J., 1925, **127**, 365; etc.). A study of methylated rhamnose and its oxidation has convinced us that the course of oxidation is normal in this case also, and that in consequence the structure of methylated rhamnose may be deduced when the nature of the oxidation products is known.

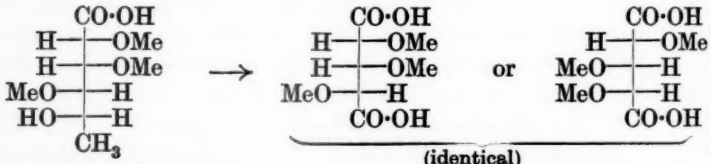
Rhamnose indeed, when methylated under various conditions, has shown a rather unusual capacity for yielding methyl derivatives of one structural form only. On methylation, either by preliminary formation of the crude mixture of α- and β-methylrhamnosides with acid methyl alcohol followed by use of the Purdie reagents, or by direct treatment with methyl sulphate, only the normal trimethyl rhamnose (Purdie and Young, J., 1906, **89**, 1194) was obtained, whereas in many cases mixtures containing both the amylene- and the butylene-oxide form of the methylated sugar are produced (Pryde, Hirst, and Humphreys, J., 1925, **127**, 348).

Oxidation of this trimethyl rhamnose by nitric acid not only showed that the compound was free from admixture with isomeric forms of different oxidic linking, but also gave a direct proof of its constitution. The oxidation product under the special conditions

adopted was *l*-arabotrimethoxyglutaric acid, which may also be obtained by oxidising trimethyl arabinose or by methylating *l*-trihydroxyglutaric acid. No methoxy-group was lost during the reaction, but the terminal methyl group was removed. These observations can be interpreted (assuming the stability of the methoxy-groups) only on the basis of an amylene-oxidic structure for normal trimethyl rhamnose, and from arguments which have been detailed previously this leads to the assigning of the amylene-oxidic formula to α- and β-methylrhamnosides and in all probability to rhamnose itself. A summary of the reactions involved is given in the accompanying scheme.



Methylrhamnoside. Trimethyl methylrhamnoside. Trimethyl rhamnose.



Trimethyl rhamnonic acid. (identical) Arabotrimethoxyglutaric acid.

The mechanism of the oxidation is in itself interesting. After the production of the intermediate trimethylrhamnonic acid, the action of nitric acid on the terminal $-CH(OH)\cdot CH_3$ group involves a quantitative transformation to $-CO\cdot OH$ and CO_2. This must proceed *via* the ketone $-CO\cdot CH_3$, and the present reaction (although not in accord with the usual behaviour of methyl ketones) is thus brought into line with certain other instances. For example, lævulic acid yields succinic acid on treatment with nitric acid (Tollens, *Annalen*, 1881, **206**, 257) and rhamnose itself gives *l*-trihydroxyglutaric acid (Will and Peters, *Ber.*, 1889, **22**, 1697). The simple nature of the change is here emphasised because of its contrast with the more complicated course of oxidation undergone by the allied group $-CH(OH)\cdot CH_2\cdot OMe$.

A study of the latter question has been completed by one of us in connexion with work on glucose, and details of this will be given in a future communication.

EXPERIMENTAL.

Methylation of Rhamnose.—A mixture of α- and β-methylrhamnosides (Fischer, *Ber.*, 1895, **28**, 1158) was methylated in the manner described by Purdie and Young (*loc. cit.*). The trimethyl α-methylrhamnoside so prepared showed the properties and physical constants given by these authors (b. p. 101°/9 mm.; $[\alpha]_D$ − 15° in water; $[\alpha]_D$ − 54° for $c = 2{\cdot}15$ in alcohol. The refractive index, hitherto unrecorded, was $n_D^{15°} = 1{\cdot}4415$).

In a second series of experiments rhamnose was treated in the usual way with methyl sulphate and caustic soda. Two such treatments followed by one with silver oxide and methyl iodide gave in good yield the fully methylated sugar as a colourless, uncrystallisable syrup, b. p. 100—101°/9 mm., $n_D^{18°}$ 1·4415 (Found: C, 54·5; H, 9·2; OMe, 55·2. Calc., C, 54·5; H, 9·1; OMe, 56·3%). It was stable to alkaline potassium permanganate solution and showed $[\alpha]_D$ − 11·3° in alcohol ($c = 1{\cdot}77$) and + 11·5° in water ($c = 2{\cdot}002$). It was therefore a mixture of the α- and β-forms of trimethyl methylrhamnoside. On hydrolysis with 8% aqueous hydrochloric acid at 90°, the specific rotation decreased regularly from the initial value of + 15·5° ($c = 1{\cdot}159$) to zero after 40 minutes and then rose gradually to a constant value, + 21·2° ($c = 1{\cdot}085$ as trimethyl rhamnose), after 200 minutes. On plotting the values against time, a curve is obtained which is characteristic of the hydrolysis of a mixture of the α- and β-forms of a methyl aldoside. Experiments on a larger scale gave a final value of + 19·5° ($c = 6{\cdot}4$) (compare Purdie and Young, *loc. cit.*). An improved method was employed to isolate the trimethyl rhamnose. After neutralisation of the acid with barium carbonate the hydrolysis product was extracted with chloroform and purified by distillation (yield 75%), being thus obtained as a colourless, viscous syrup, b. p. 141°/19 mm. (bath at 153°), $n_D^{15°}$ 1·4565 (Found: C, 52·3; H, 8·7; OMe, 44·7. Calc., C, 52·4; H, 8·7; OMe, 45·1%). $[\alpha]_D$ + 24·9° (in water, $c = 2{\cdot}53$), − 9° (in alcohol, $c = 1{\cdot}36$). It was obviously identical with the trimethyl rhamnose prepared by Purdie and Young.

Oxidation of Trimethyl Rhamnose.—A solution of 3·0 g. of trimethyl α-methylrhamnoside (prepared from α-methylrhamnoside; or trimethyl rhamnose may be used) in 70 c.c. of nitric acid (d 1·2) was heated slowly until oxidation commenced, at 85°. The reaction proceeded vigorously and was apparently complete after 4 hours. Heating was then renewed, and continued for a further 2½ hours. The oxidation product was freed from nitric acid, dried, and esterified with acid methyl alcohol by the method described in previous papers of this series. The ester (2·61 g. or 77% of the

theoretical yield) was purified by distillation and thus obtained as a colourless, uncrystallisable syrup [2·41 g.; b. p. 135°/9 mm. (bath at 150°); $n_D^{20°}$ 1·4350; $[\alpha]_D + 47·6°$ (in methyl alcohol, $c = 1·706$)]. It behaved as an ester on titration, and analysis and a comparison of its physical constants with those of an authentic sample prepared from arabinose showed it to be dimethyl *l*-arabotrimethoxyglutarate ($n_D^{21°}$ 1·4355; b. p. 143°/18 mm.; $[\alpha]_D + 47·3°$ for $c = 1·842$ in methyl alcohol) [Found: C, 47·8; H, 7·25; OMe, 60·2; CO_2Me (by hydrolysis), 46·3. Calc., C, 48·0; H, 7·2; OMe, 62·0; CO_2Me, 47·2%]. In view of the large difference in rotatory power between the acid and its fully methylated dimethyl ester (Hirst and Robertson, *loc. cit.*), it was of interest to examine the rotation of the sodium salt. A weighed quantity of the ester was hydrolysed with just more than the calculated quantity of caustic soda, and the solution was exactly neutralised with hydrochloric acid; $[\alpha]_D + 25°$ was thus found for the sodium salt (compare Purdie and Irvine, J., 1901, **79**, 962, for the rotations of dimethyl *d*-dimethoxysuccinate and the corresponding sodium salt).

When the ester was treated with methyl alcohol saturated with dry ammonia (0·36 g. in 3·6 c.c.), crystals of the diamide separated after 15 hours, and after 3 days 0·20 g. was collected (63% yield). The crystals were washed with cold methyl alcohol and ether and recrystallised once from methyl alcohol; they then had m. p. 230°, alone or mixed with an authentic specimen of *l*-arabotrimethoxyglutardiamide. The solubilities, the crystalline form, the behaviour on heating, and the specific rotation of this substance were in exact agreement with those previously recorded. $[\alpha]_D + 50·4°$ ($c = 0·6942$ in water) (Found: OMe, 41·6. Calc., OMe, 42·3%).

ARMSTRONG COLLEGE, NEWCASTLE UPON TYNE, AND DEPARTMENT OF SCIENCE, DURHAM,
UNIVERSITY OF DURHAM. [*Received, November 20th,* 1925.]

VII.—*The Specific Heats of Hydrocyanic Acid. A Reply.*

By EDITH HILDA INGOLD.

EARLY this year, a paper by Partington and Carroll appeared (*Phil. Mag.*, 1925, **49**, 665) dealing with the ratio of the specific heats of hydrocyanic acid. The author's previous measurements of this constant (J., 1922, **121**, 1604) were discussed at some length and criticised on two distinct grounds.

The first of these criticisms is summed up in the remark that "the results obtained by Usherwood, although interesting and useful, are approximate only." * Since results of moderate precision were all that the author attempted to obtain, no exception could be taken to this statement were it not made in association with comments relating to the author's experimental procedure which are without foundation in fact, and are apparently intended to suggest a want of care. Thus, Partington and Carroll state: "The gas used, obtained by the action of dilute sulphuric acid on potassium cyanide,† scarcely fulfils the purity requirements required for the determination of physical constants." It was, however, made clear in the original experimental description (*loc. cit.*, p. 1609), and may again be emphasised, that the "gas used" was not, as this sentence implies, taken *straight from the generating apparatus into the sound-tube*, but was *first liquefied*, dried, fractionated until its boiling point was constant, and frozen, before use. A specimen of hydrocyanic acid, prepared by this method, has recently been sent for the determination of physical constants to another worker, who reports that he has found it satisfactory. Another similar criticism is that the author made no mention of "precautions taken to prevent contamination of the vapour by air, due to leakage into the apparatus." It is true that since the elementary precaution of ensuring that an apparatus is gas-tight is not peculiar to the experiments described, it was omitted from the experimental description. It may now be stated, however, (*a*) that the apparatus *was* tested for leakage before and after every experiment, (*b*) that (excepting in preliminary experiments which were not published) no leakage was found, (*c*) that the arrangement was such that if there had been a leak hydrocyanic acid would have passed into the air, not *vice versa*.

The second main criticism offered by Partington and Carroll is that the results obtained by the author are due not, as was suggested, to the thermal effect accompanying isomeric change, but to the thermal effect accompanying polymerisation, the occurrence of which, in the vapour of hydrocyanic acid, is, according to Partington and Carroll, indicated by the author's measurements of its density.

* This conclusion is not, as might perhaps be thought, based on any obvious disagreement between the author's results and those of Partington and Carroll; nor do these authors claim that their measurements are of superior precision, although they may well be, having evidently been conducted with great care and attention to detail. They were carried out at the ordinary temperature and under reduced pressures, whereas the author's observations were made at elevated temperatures.

† It was actually pure sodium cyanide, as appears from the description given (*loc. cit.*, p. 1609).

These measurements showed that, although above about 170°, the density is normal (ideal) to within the limits of experimental error (estimated as 0·2%), on approaching the point of liquefaction substantially higher densities obtain, the value at the lowest temperature investigated being nearly 4% above the theoretical. This type of behaviour is, of course, well known. Vapour densities about 3—6% higher than the theoretical were observed by S. Young (*Proc. Roy. Soc. Dublin*, 1910, **12**, 374) for a great variety of substances, including many, such as fluorobenzene, benzene, hexane, pentane, etc., which could not be suspected of any noteworthy tendency to polymerise. The inert gases exhibit the same characteristic. Partington and Carroll, however, regard such density values as indicating in the case of hydrocyanic acid, not deviations from the gas laws, that is, deviations due to molecular attraction and molecular size (the a and b of van der Waals), but polymerisation. Thus the observed 4% excess over the theoretical density is interpreted as indicating that approximately 8% of the molecules have combined to form $(HCN)_2$. This view of vapour density results appears to the author entirely contrary to accepted principles. If it were valid, the continuity of state would demand that compressed gases and even ordinary liquids (the densities of which at $N.T.P$ may be thousands of times their ideal vapour densities) must consist principally of enormously polymerised molecules; indeed there would be no such thing as a non-associated liquid. In contradistinction to this view, the author wishes to maintain that, since hydrocyanic acid behaves, in regard to vapour density, similarly to numerous other substances, including inert gases and paraffin hydrocarbons, which are non-associated *even in the liquid state*, and can therefore safely be assumed to be non-associated as vapour, the densities observed in the case of hydrocyanic acid vapour near the point of liquefaction are to be interpreted, not as proving association, but as effects due to departure from the condition (point-molecules without attraction) imagined in an ideal gas. Partington and Carroll refer to the " association " of water vapour as an established fact, and certainly, since liquid water is markedly associated, its vapour would be expected to afford a particularly favourable case for the detection of association in the gaseous state. Yet Kendall (*J. Amer. Chem. Soc.*, 1920, **42**, 2477; compare Menzies, *ibid.*, 1921, **43**, 851) has proved conclusively that, despite its enhanced density, the degree of association of water vapour, if not zero, is at any rate so small that the most accurate available measurements fail to show it. Numerous other cases in which density results had previously been interpreted as indicating association in the vapour have been shown by Kendall and Menzies

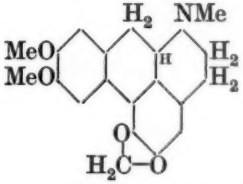
to be completely accounted for by deviations from the gas laws.*

THE UNIVERSITY, LEEDS. [*Received, November 5th*, 1925.]

VIII.—*Resolution of* dl-*Dicentrine.*

By ROBERT DOWNS HAWORTH, WILLIAM HENRY PERKIN, jun., and JOHN RANKIN.

IN a previous communication (J., 1925, **127**, 2018), the synthesis of a *dl*-base, $C_{20}H_{21}O_4N$, having the constitution



suggested by Gadamer (*Arch. Pharm.*, 1911, **249**, 701) for dicentrine is described and it was pointed out that the synthetical base exhibits a series of colour reactions identical with those described by Asahina (*Arch. Pharm.*, 1909, **247**, 206) as characteristic of naturally occurring *d*-dicentrine. It has now been found that the *dl*-base may be readily resolved into its *d*- and *l*-modifications by means of tartaric acid under conditions similar to those employed by Gadamer (*loc. cit.*, p. 688) for the resolution of *dl*-glaucine. The *d*- and *l*-modifications crystallise well from ether, melt at 169°, and have $[\alpha]_D + 64{\cdot}1°$ and $- 63{\cdot}5°$, respectively.

* Partington and Carroll calculate that at the critical point hydrocyanic acid must "consist almost entirely of double molecules." On similar principles, argon at the critical point should mainly consist of A_3. On the other hand, the possibility of association near the critical point (*i.e.*, under high pressure) must be admitted in the case of substances which are associated as liquids, and hence critical data must be used with caution in such cases.

Partington and Carroll's remaining criticisms relate principally to the author's method of calculating the results. For instance, they propose correcting for the variation with temperature of the specific heats of air; a correction which was omitted, since it makes a difference of only about 3 units in the fourth significant figure. They also suggest an alternative method (based on "calculated" critical data) for correcting for deviations from the gas laws, but later in their paper declare it to be unjustified for the reason given above. Bredig and Teichmann (*Z. Elektrochem.*, 1925, **31**, 449) observed critical data in fairly good agreement with those used by Partington and Carroll, but near the critical point a curved "rectilinear diameter" was obtained, which may indicate appreciable association under these conditions (Guye, *Arch. Sci. phys. nat.*, 1894, **31**, 38).

These constants agree closely with those assigned to dicentrine by Asahina (*loc. cit.*; m. p. 168—169°; $[\alpha]_D$ + 62·7°) and a direct comparison of the *d*-base with a specimen of *d*-dicentrine which Professor Gadamer kindly sent us definitely established identity.

Experimental.

dl-Dicentrine was prepared in the way described in our earlier communication (*loc. cit.*). Commencing with 30 g. of homoveratroylhomopiperonylamine, 7·5 g. of the dihydrochloride of 6′-aminoveratrylhydrohydrastinine were obtained and this yielded 1·3 g. of pure *dl*-dicentrine, m. p. 181° (corr.).

In an attempt to devise an alternative method for the preparation of 6′-nitroveratrylhydrohydrastinine, 6′-nitroveratrylnorhydrohydrastinine (1·5 g.), water (7 c.c.), 40% formalin (0·5 c.c.), and anhydrous formic acid (0·8 c.c.) were heated for 6 hours at 160—170° in a sealed tube. The contents of the tube were diluted with water, and the pale yellow needles collected and recrystallised from alcohol (m. p. 119°) and identified as 6-nitrohomoveratrole. The acid solution was made alkaline with sodium hydroxide, allowed to remain for 24 hours, the precipitate collected, washed with water and crystallised from petroleum (b. p. 40—60°), separating in colourless plates, m. p. 56—58° (Found: C, 68·9; H, 6·7. Calc. for $C_{11}H_{13}O_2N$, C, 69·1; H, 6·8%). The identity of this substance with hydrohydrastinine was confirmed by the preparation of the methiodide, which crystallised from methyl alcohol in colourless, rhombic prisms, m. p. 229°, and by the fact that on oxidation with iodine a solution was obtained which exhibited the characteristic hydrastinine fluorescence. The formation of 6-nitrohomoveratrole and hydrohydrastinine under the influence of formaldehyde and formic acid involves a reduction, a methylation, and a scission of the molecule of a kind similar to that observed by Hope and Robinson (J., 1911, **99**, 2114) when they obtained 2 · 6-dinitrotoluene and cotarnine by heating anhydrocotarnine-2 : 6-dinitrotoluene with glacial acetic acid.

Resolution of dl-*Dicentrine.*—A 2*N*-absolute alcoholic solution of *d*-tartaric acid (0·6 c.c.) was added slowly to a solution of *dl*-dicentrine (0·5 g.) in absolute alcohol (25 c.c.) until a faint acid reaction was observed towards litmus. The clear tartrate solution was converted into the hydrogen tartrate by the gradual addition of a further quantity of *d*-tartaric acid (0·6 c.c.); an amorphous precipitate then separated which redissolved on gently warming. On vigorously scratching, *l*-dicentrine hydrogen *d*-tartrate (0·2 g.) separated from the warm solution in small crystals which, after cooling, were collected and washed with alcohol.

The filtrate and washings were evaporated to dryness, the gummy residue dissolved in water, the bases liberated by the addition of sodium hydroxide, extracted with ether, the extract dried, and the ether removed. The residue (0·37 g.) was dissolved in absolute alcohol (20 c.c.) and titrated with a 2*N*-absolute alcoholic solution of *l*-tartaric acid (0·45 c.c.) * until a faint acid reaction was obtained. The clear solution was then treated with a further quantity of *l*-tartaric acid (0·45 c.c.); an amorphous precipitate then separated which redissolved on gently warming. *d*-Dicentrine hydrogen *l*-tartrate (0·2 g.) separated, on scratching, as a crystalline powder, which was collected and washed with alcohol.

The salts in the filtrate and washings were reconverted into base and the treatment with *d*- and *l*-tartaric acid was repeated under the same conditions, when further quantities of *l*-dicentrine hydrogen *d*-tartrate (0·1 g.) and *d*-dicentrine hydrogen *l*-tartrate (0·1 g.) were obtained.

Both l-*dicentrine hydrogen* d-*tartrate* and d-*dicentrine hydrogen* l-*tartrate* are soluble in water but almost insoluble in alcohol, and both crystallise from alcohol containing a little water in colourless, nodular masses.

d-*Dicentrine* was obtained by dissolving the recrystallised *d*-dicentrine hydrogen *l*-tartrate in water, making slightly alkaline with sodium hydroxide, extracting with ether, drying over anhydrous sodium sulphate, and concentrating the filtered ethereal solution, when *d*-dicentrine separated in long, colourless prisms, m. p. 169° (corr.). When mixed with a specimen of the *d*-dicentrine obtained from Professor Gadamer, no alteration in m. p. was observed. In chloroform solution: $l = 1$, $c = 1{\cdot}433$; $\alpha_D^{17^\circ} = 0{\cdot}92°$, whence $[\alpha]_D^{17^\circ} = +\,64{\cdot}1°$. *d*-Dicentrine is readily soluble in alcohol, ethyl acetate, and benzene, almost insoluble in petroleum, and is more soluble in ether than *dl*-dicentrine. It is readily soluble in chloroform, the solution gradually becoming yellow (compare Asahina, *loc. cit.*). The recovery of the base from the chloroform solutions used for optical measurements is a wasteful process, because when the solutions are concentrated a double compound insoluble in ether separates. This can be decomposed by the addition of a little methyl-alcoholic potassium hydroxide and the *d*-dicentrine crystallised from ether, when it is recovered as prisms (m. p. 169°), which, however, are always yellow.

l-*Dicentrine* was obtained from recrystallised *l*-dicentrine hydrogen *d*-tartrate exactly as described in the case of the *d*-base. It crystallises from ether in long, colourless prisms, m. p. 169°

* Our thanks are due to Sir W. J. Pope for the *l*-tartaric acid used in these experiments.

(corr.). When mixed in about equal proportions with a specimen of *d*-dicentrine, the mixture softens at 168°, but does not melt completely until about 178°. In chloroform: $l = 1$, $c = 1{\cdot}700$, $\alpha_D^{17°} = -1{\cdot}08°$, whence $[\alpha]_D^{17°} = -63{\cdot}5°$. *l*-Dicentrine resembles the *d*-base in its behaviour towards solvents and is recovered as yellow prisms, m. p. 169°, from a chloroform solution.

One of us (R. D. H.) is indebted to the Commissioners of the 1851 Exhibition for a studentship which has enabled him to take part in this research, and to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of the investigation

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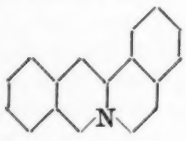
IX.—*Synthetical Experiments in the* iso*Quinoline Group. Part VI. A Synthesis of Derivatives of Paraberine.**

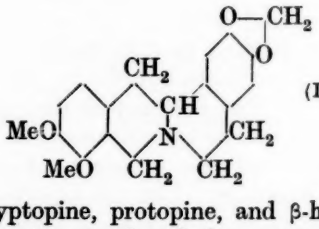
By RAY CAMPBELL, ROBERT DOWNS HAWORTH, and WILLIAM HENRY PERKIN, jun.

THE careful investigation of the alkaloids of the palmatine, berberine, corydaline type has not only demonstrated their *iso*quinoline structure, but has also shown that they are all built up on the same curious "angular" skeleton (I), a point which is made clear when the formula of berberine or, still better, of tetrahydroberberine (II) is written alongside.

(I.)

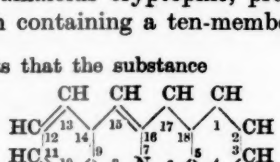


(II.)



Furthermore, the alkaloids cryptopine, protopine, and β-homochelidonine, although containing a ten-membered ring, are readily

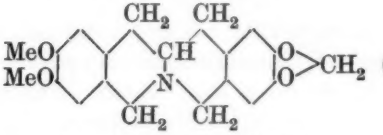
* The Editor suggests that the substance



should be named "*paraberine*."

converted into quaternary salts, such as *iso*cryptopine chloride, which again are derived from the skeleton (I). It is not clear why this particular angular structure should be selected as the basis of so many of the naturally occurring alkaloids, unless indeed it be that substances of this type are particularly amenable to synthesis. In order to obtain evidence on this point, it appeared to us that it would be of interest to synthesise an alkaloid of the paraberine type containing in the place of (I) the " linear " skeleton (III) and to compare the ease of formation and general properties of such a substance with those of the alkaloids met with in nature.

(III.)

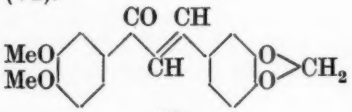


(IV.)

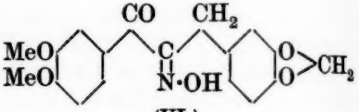
It will be seen from the experimental section of this communication that, although we were ultimately successful in constructing an alkaloid (IV) derived from the skeleton (III), the smallness of the yields at several stages made the completion of the synthesis a particularly difficult one. It is quite clear to us that substances of the angular type (I) are much more readily synthesised, under the conditions we have employed in this series of researches, than those of the linear type (III), and this fact may have some bearing on the occurrence of the angular type in nature. In attempting to synthesise (IV), the most obvious starting point was 6 : 7-dimethoxy-4-dihydro*iso*quinolone, $C_6H_2(OMe)_2\langle\begin{matrix}CO-CH_2\\CH_2\cdot NH\end{matrix}$, but we were unable to obtain this substance either from ω-aminoacetoveratrone, $(MeO)_2C_6H_3\cdot CO\cdot CH_2\cdot NH_2$, by the action of formalin or from the *N*-formyl derivative of the base by treatment with phosphorus oxychloride. Moreover, *N*-phenacetyl-ω-aminoacetoveratrone (Robinson, J., 1909, **95**, 2167), on treatment with phosphorus oxychloride, yielded not the *iso*quinoline derivative but 5-veratryl-2-benzyloxazole (m. p. 86°), which Robinson had obtained from the phenacetyl derivative by the action of sulphuric acid. This failure to close the *iso*quinoline ring seems to indicate that it is the carbonyl group in ω-aminoacetoveratrone which inhibits ring formation, because when this group is replaced by $>CH_2$ or $>CH\cdot OH$ *iso*quinoline derivatives may be readily obtained (Pictet and Gams, *Ber.*, 1909, **42**, 2943; Decker, *Annalen*, 1913, **395**, 299). After many other unsuccessful attempts, we ultimately succeeded, with the aid of the following scheme, in synthesising 2 : 3-*methylenedioxy*-11 : 12-*dimethoxy*-6 : 15 : 16 : 17-*tetrahydroparaberine* (IV).

3 : 4-Dimethoxyphenyl 3 : 4-methylenedioxystyryl ketone (V),

prepared from acetoveratrone and piperonal by Bargellini and Monti's method (*Gazzetta*, 1914, **44**, ii, 25), was reduced by hydrogen in the presence of colloidal palladium to 3 : 4-*dimethoxyphenyl* 3 : 4-*methylenedioxy*-β-*phenylethyl ketone*, which, on treatment with methyl nitrite and sodium ethoxide, yielded the iso*nitroso*-derivative (VI).



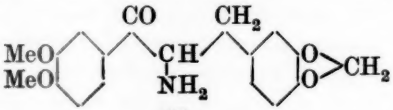
(V.)



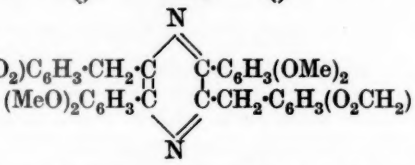
(VI.)

The reduction of this *iso*nitroso-derivative to 3 : 4-*dimethoxyphenyl* 3 : 4-*methylenedioxy*-β-*phenyl*-α-*aminoethyl ketone* (VII) proved to be a troublesome operation. When alkaline reducing agents were employed, the pyrazine derivative (VIII) was produced as the result of condensation between two molecules of the base (VII) followed by spontaneous oxidation. Eventually the amine (VII) was obtained by reducing the *iso*nitroso-derivative (VI) with stannous chloride, but in order to obtain even approximately good yields the conditions described on p. 38 must be exactly followed.

(VII.)

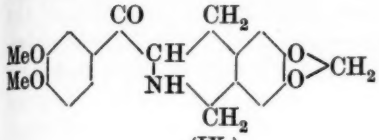


(VIII.)

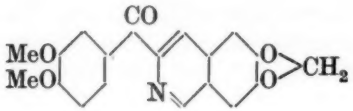


The amine (VII) condenses readily with formalin and hydrochloric acid to give 6 : 7-*methylenedioxy*-3-(3′ : 4′-*dimethoxybenzoyl*)-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (IX), the *hydrochloride*, *oxime*, *picrate*, and *benzoyl* derivative of which have been prepared. When the base (IX) is oxidised with iodine, it is converted into 6 : 7-*methylenedioxy*-3-(3′ : 4′-*dimethoxybenzoyl*)isoquinoline (X), which is closely related to papaveraldine in structure and properties. It is a weak tertiary base yielding pale yellow salts which are slowly dissociated by water. On fusion with potassium hydroxide, it is decomposed and veratric acid has been isolated from the product, but the basic residue could not be identified, as it was no doubt destroyed during the fusion owing to disruption of the methylenedioxy-group. The formation of veratric acid is, however, welcome confirmation of the validity of the structures (IX) and (X) and it is evident that when the amine (VII) is condensed with formalin it

is again the >CO group which inhibits ring closure with the veratryl nucleus.

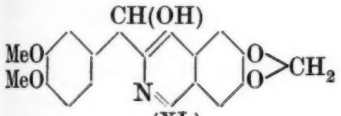


(IX.)

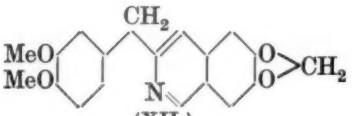


(X.)

The base (X), on reduction with zinc dust and acetic acid, yields 6 : 7-*methylenedioxy*-3-(α-*hydroxy*-3′ : 4′-*dimethoxybenzyl*)iso*quinoline* (XI), a secondary alcohol which shows reactions similar to those of papaverinol. When treated with hydrobromic acid and zinc dust (compare Buck, Perkin, and Stevens, J., 1925, **127**, 1471), it yielded an oily base the crystalline picrate of which gave analytical figures agreeing with those required for the *picrate* of 6 : 7-*methylenedioxy*-3-(3′ : 4′-*dimethoxybenzyl*)iso*quinoline* (XII), but owing to the small amount of material at our disposal we were unable to isolate the base in a pure state.



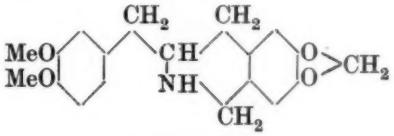
(XI.)



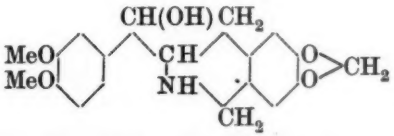
(XII.)

The reduction of the substances (IX), (X), and (XI) to 6 : 7-*methylenedioxy*-3-(3′ : 4′-*dimethoxybenzyl*)-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (XIII) proved to be a very difficult operation. Reducing agents such as sodium amalgam, zinc and sulphuric acid, as well as electrolytic reduction in the cold, led to the formation of amorphous bases. Since an exactly similar series of substances was obtained from papaveraldine and papaverinol under the same conditions, we are of the opinion that these amorphous bases are of the type (XIV).

(XIII.)



(XIV.)

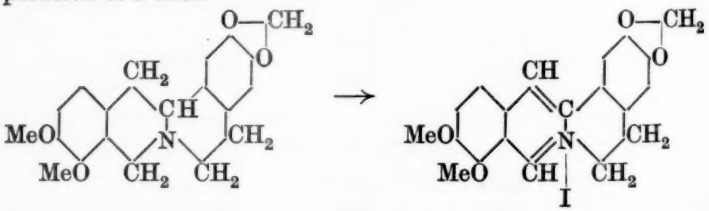


Freund and Beck (*Ber.*, 1904, **37**, 3321) obtained an amorphous base, which they named "*iso*tetrahydropapaverine," by the electrolytic reduction of papaveraldine in hot dilute sulphuric acid,

but Pyman (J., 1909, **95**, 1610) showed that their base is identical with tetrahydropapaverine prepared by reducing papaverine with tin and hydrochloric acid. We have confirmed the identity of the two preparations by a careful comparison of the hydrochlorides, hydriodides, and nitrosoamines. When we applied the conditions employed by Freund and Beck to the electrolysis of the substance (X), we obtained the base (XIII) corresponding with tetrahydropapaverine. It is remarkable that this also is amorphous, but it yields a well-crystallised *hydrochloride*, *hydriodide*, and *nitrosoamine*.

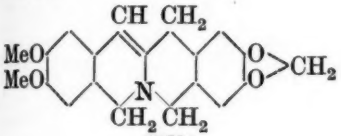
The base (XIII) is converted into 2 : 3-*methylenedioxy*-11 : 12-*dimethoxy*-6 : 15 : 16 : 17-*tetrahydroparaberine* (IV) by the action of formalin and hydrochloric acid, but the yield is extremely small and modifications of the process did not lead to any improvement. This experience appears to indicate that the system of rings (III) is produced only with difficulty and when compared with the ease of formation of substances of the tetrahydroberberine type under the same conditions clearly emphasises the greater tendency towards angular ring formation (I) (compare Lellmann and Schmidt, *Ber.*, 1887, **20**, 3154; von Braun, *ibid.*, 1922, **55**, 1710; Mayer and Schnecko, *ibid.*, 1923, **56**, 1408).

In spite of the poor yield we have been able to examine the properties of the base (IV) in some important directions. It was to be expected that, owing to analogy in constitution, the base (IV) would exhibit properties closely allied to those of tetrahydroberberine and still more to those of tetrahydro-ψ-berberine (Haworth, Perkin, and Rankin, J., 1924, **125**, 1696). The latter two are characterised by the facility with which they crystallise as well as by the sparing solubility of their salts. But the most striking characteristic is their behaviour on oxidation with iodine, when they yield quaternary salts such as berberinium iodide or ψ-berberinium iodide (*loc. cit.*, p. 1698) which are not decomposed by alkali with separation of a base.

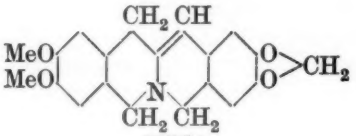


2 : 3-Methylenedioxy-11 : 12-dimethoxy-6 : 15 : 16 : 17-tetrahydroparaberine (IV; m. p. 222°) resembles tetrahydroberberine (m. p. 168°) and tetrahydro-ψ-berberine (m. p. 177°) in being rather sparingly soluble and yielding sparingly soluble, beautifully crystalline salts. The *methiodide* (m. p. 268°), like tetrahydroberberine

methiodide (m. p. 251°) and tetrahydro-ψ-berberine methiodide (m. p. 260°), exhibits remarkable stability to boiling alcoholic potassium hydroxide. On the other hand, when it is treated with iodine, base (IV) does not undergo a change corresponding with the conversion of tetrahydro-berberine or -ψ-berberine into the quaternary berberinium salts. The product consists mainly of a bright yellow, crystalline *hydriodide*, $C_{20}H_{19}O_4N,HI$, from which the corresponding *hydrochloride* is obtained by the action of silver chloride, and the latter, in contact with ammonia, is immediately decomposed with separation of an amorphous base, $C_{20}H_{19}O_4N$, which is clearly a 2 : 3-*methylenedioxy*-11 : 12-*dimethoxydihydroparaberine* (6 : 17 or 6 : 15) having one or other of the constitutional formulæ (XV and XVI).



(XV.)



(XVI.)

The reason for this difference in behaviour is difficult to understand, since the formula of base (IV) contains the grouping which is responsible for the formation of berberinium salts in the berberine series.

Experimental.

3 : 4-*Dimethoxyphenyl* 3 : 4-*Methylenedioxy*-β-*phenylethyl Ketone*.—3 : 4-Dimethoxyphenyl 3 : 4-methylenedioxystyryl ketone (V) was obtained in quantitative yield from piperonal and acetoveratrone under the conditions described by Bargellini and Monti (*loc. cit.*), but in reducing large quantities of this substance the following method is more suitable than that of the above-mentioned investigators. The styryl ketone (50 g.), glacial acetic acid (500 c.c.), 3% palladium chloride (15 c.c.), and gum arabic (0·5 g. in a little water) were introduced into a flask, connected to the hydrogen supply and immersed in a water-bath at 50—60°. The flask was fitted with a vigorously acting air-tight mechanical stirrer, the air displaced, and the mixture stirred, when a rapid absorption of hydrogen took place for 2 hours. The hot, colourless solution was filtered, most of the solvent removed, with the aid of a column, under diminished pressure, and methyl alcohol added, when the residue set to a mass of white crystals (41 g.); these crystallised from methyl alcohol in white, woolly needles, m. p. 102—103° (B. and M., *loc. cit.*, give 98—100°). The *oxime*, prepared by boiling the phenylethyl ketone with potassium acetate and hydroxylamine hydrochloride in alcoholic solution, crystallised from aqueous alcohol in slender needles, m. p.

119—121°. The *iso*nitroso-derivative (VI) was obtained by adding the phenylethyl ketone (10 g.) to boiling alcohol (200 c.c.) in which sodium (2·5 g.) had been dissolved. The hot solution was treated with a stream of dry methyl nitrite (Slater, J., 1920, **117**, 587), cooled, completely saturated with methyl nitrite, and kept in a stoppered flask for 12 hours at the room temperature, when a small amount of solid separated. Most of the alcohol was removed under diminished pressure, the residue diluted with water, and impurities extracted with benzene. Air was drawn through the aqueous layer, which was then rendered slightly acid with acetic acid, the precipitate collected,* dried (8 g.), and crystallised from aqueous acetic acid, separating in colourless needles, m. p. 137° (Found: C, 62·9; H, 5·1; N, 4·3. $C_{18}H_{17}O_6N$ requires C, 62·9; H, 5·0; N, 4·1%). This *iso*nitroso-derivative is soluble in alcohol, chloroform, or ethyl acetate, slightly soluble in ether, and sparingly soluble in water or petroleum. An attempt to reduce it with zinc dust and acetic acid at 60° led to the regeneration of the phenylethyl ketone (m. p. 102—103°).

3 : 4-*Dimethoxyphenyl* 3 : 4-*Methylenedioxy*-β-*phenyl*-α-*aminoethyl Ketone* (VII).—Anhydrous stannous chloride (56 g.) dissolved in absolute alcohol (300 c.c.) was saturated with dry hydrogen chloride at −10°, the finely powdered *iso*nitroso-derivative (40 g.) added, and the solution again saturated with hydrogen chloride at −10°. After remaining over-night, the crystalline *stannichloride* of the base (VII) which had separated was collected, dissolved in water, decomposed with hydrogen sulphide, filtered, and the filtrate concentrated until the hydrochloride separated as an oil which rapidly hardened. This (40 g.) was crystallised from a mixture of alcohol and ether, separating in slender, colourless needles, m. p. 218—219° (decomp.) (Found: C, 59·5; H, 5·5. $C_{18}H_{18}O_5N,HCl$ requires C, 59·9; H, 5·5%). This *hydrochloride* is sparingly soluble in cold alcohol, but dissolves readily in water or warm alcohol. The *picrate* was prepared in alcoholic solution and crystallised from alcohol in yellow needles, m. p. 213° (Found: C, 51·7; H, 4·1. $C_{24}H_{22}O_{12}N_4$ requires C, 51·6; H, 3·9%). When sodium hydroxide is added to the aqueous solution of the hydrochloride, a turbid solution is first produced and after some time a brown, sticky solid separates which is evidently produced by the base undergoing condensation and oxidation to the pyrazine (VIII).

The *pyrazine* (VIII) is best prepared by stirring a solution of the *iso*nitroso-derivative (VI) in sodium hydroxide with zinc dust

* The mother-liquors contain a little *iso*nitroso-compound together with some veratric acid, evidently produced by the hydrolysis of some of the *iso*nitroso-derivative.

for 3 hours at the room temperature. The sticky solid which separates is extracted with chloroform, dried, the solvent removed, and the syrup crystallised from a mixture of alcohol and chloroform, when pale yellow needles, m. p. 205°, are obtained (Found : C, 69·0; H, 5·2. $C_{36}H_{32}O_8N_2$ requires C, 69·6; H, 5·2%). This *pyrazine* is insoluble in alkali and is a weak base dissolving in concentrated hydrochloric acid, from which it is precipitated by dilution with water.

6 : 7 - *Methylenedioxy*-3 - (3′ : 4′-*dimethoxybenzoyl*)-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (IX).—A solution of the hydrochloride of the amine (VII) (2 g.) in methyl alcohol (25 c.c.) and 40% formalin (5 c.c.) was decomposed with sodium bicarbonate, boiled for 20 minutes, diluted with water, and the reddish-brown condensation product collected, washed free from formalin, and digested on the steam-bath with 20% hydrochloric acid. The mass dissolved and in a few minutes the hydrochloride of the base (IX) began to separate, the quantity increasing during 20 minutes. The mixture was cooled, the hydrochloride collected, washed with water, and recrystallised from very dilute hydrochloric acid. It was then dissolved in water and the base liberated by the addition of ammonia, collected, and crystallised from ethyl alcohol, from which it separates in rosettes of almost colourless needles, m. p. 137° (Found : C, 67·2; H, 5·7. $C_{19}H_{19}O_5N$ requires C, 66·9; H, 5·5%). The *base* (IX) is readily soluble in chloroform, acetone, hot alcohol, or hot benzene, and sparingly soluble in ether, petroleum, cold alcohol, or cold benzene. It dissolves in concentrated sulphuric acid to a pale yellow solution, which becomes blood-red on the addition of a crystal of potassium nitrate. The *hydrochloride* crystallises from very dilute hydrochloric acid in slender needles containing water of crystallisation, which is lost at 115—120°. The hydrated salt is very soluble in alcohol and the addition of ether to an alcoholic solution precipitates the anhydrous hydrochloride in fine needles, m. p. 232—234° (decomp.), which are now insoluble in alcohol. The hydrated salt dried at 120° lost 9·7% H_2O; $C_{19}H_{20}O_5NCl,2H_2O$ requires H_2O, 8·7% (Found : C, 60·0; H, 5·5. $C_{19}H_{20}O_5NCl$ requires C, 60·4; H, 5·3%). The *benzoyl* derivative, obtained by the action of benzoyl chloride and sodium hydroxide on a solution of the hydrochloride, crystallises from alcohol in long, slender needles, m. p. 187—188° (Found : C, 69·7; H, 5·2. $C_{26}H_{23}O_6N$ requires C, 70·1; H, 5·2%). The *picrate*, prepared from an alcoholic solution of the hydrochloride, crystallises from alcohol in yellow needles containing solvent of crystallisation, m. p. 157—158° (decomp.) (Found : C, 50·9; H, 4·5. $C_{25}H_{22}O_{12}N_4,H_2O$ requires C, 50·9; H, 4·1%). The *oxime* was obtained by heating the hydro-

chloride with hydroxylamine hydrochloride for 1 hour in pyridine solution. The mixture was diluted with water and saturated with carbon dioxide; the oxime then slowly separated in needles, m. p. 205—209° (decomp.).

6 : 7-*Methylenedioxy*-3-(3′ : 4′-*dimethoxybenzoyl*)iso*quinoline* (X).—The base (IX) (2 g.) was dissolved in ethyl alcohol (50 c.c.) containing potassium acetate (2 g.) and the solution boiled for ½ hour during the gradual addition of a 2% alcoholic solution of iodine (200 c.c.). On cooling, a mass of crystals separated which were collected, washed with sulphurous acid, water, and alcohol and crystallised from 50% alcoholic glacial acetic acid, separating in colourless needles, m. p. 222° (Found: C, 67·1; H, 4·5. $C_{19}H_{15}O_5N$ requires C, 67·6; H, 4·4%). This substance (X) is sparingly soluble in alcohol, but readily soluble in glacial acetic acid or chloroform. It is insoluble in water, but dissolves in warm dilute hydrochloric acid to a yellow solution, from which the free base separates on cooling. The *sulphate* crystallises from 20% sulphuric acid in pale yellow plates which slowly dissociate on washing with water. The *oxime* was obtained by boiling an alcoholic solution of the base (X) with hydroxylamine hydrochloride and potassium acetate for 8 hours. The solid was collected and washed with water, when the oxime remained as slender, colourless needles, m. p. 234—236° (decomp.). The base (X) (1 g.) was fused at 180° with potassium hydroxide (10 g.) and a little water. After 5 minutes the brown mass was dissolved in water, the black solution saturated with carbon dioxide, and the brown, amorphous precipitate collected. The filtrate was acidified, extracted with chloroform, the extract dried, and the solvent removed, when a brown solid remained. This was warmed with sodium bicarbonate solution, filtered, the filtrate acidified, the solid collected and crystallised from hot water containing animal charcoal, when needles, m. p. 178°, were obtained which were identified as veratric acid.

6 : 7-*Methylenedioxy*-3-(α-*hydroxy*-3′ : 4′-*dimethoxybenzyl*)iso*quinoline* (XI).—The substance (X) (2 g.) dissolved in glacial acetic acid (20 c.c.) was heated on a water-bath during the gradual addition of zinc dust (0·4 g.). After 4 hours, the solution was filtered, the filtrate diluted with water, allowed to remain for some time, and the small precipitate of unchanged (X) removed. The filtrate was saturated with hydrogen sulphide, the zinc sulphide removed, the filtrate concentrated and made alkaline with concentrated ammonia, when a sticky solid separated which gradually hardened. This was collected, and crystallised from alcohol in colourless needles, m. p. 153° (Found: C, 67·4; H, 5·1. $C_{19}H_{17}O_5N$ requires C, 67·3; H, 5·0%). This base (XI) is insoluble in water, sparingly soluble

in cold alcohol, but readily soluble in hot alcohol, acetone, or chloroform. It dissolves in concentrated sulphuric acid to a magenta-coloured solution, which becomes deep green on the addition of a crystal of potassium nitrate. The *picrate* separated as an oil which rapidly hardened when an alcoholic solution of the base (XI) was treated with picric acid. It crystallises from much alcohol in yellow needles which darken at 183° and melt at 195° (decomp.) (Found: C, 53·1; H, 3·7. $C_{25}H_{20}O_{12}N_4$ requires C, 52·8; H, 3·5%).

6:7-*Methylenedioxy*-3-(3′:4′-*dimethoxybenzyl*)*isoquinoline* (XII).—The base (XI) (0·5 g.) was allowed to remain for 12 hours in glacial acetic acid (5 c.c.) saturated with hydrogen bromide. The solution was then heated to 30°, stirred, and excess of zinc dust added slowly during 3 hours. After filtration, the solution was diluted with water (50 c.c.), made alkaline with ammonia, extracted with chloroform, the extract dried and concentrated, when a thick syrup was obtained which did not crystallise. The *picrate* was prepared in alcoholic solution and crystallised from much alcohol in yellow needles, m. p. 206—207° (Found: C, 53·9; H, 3·7. $C_{25}H_{20}O_{11}N_4$ requires C, 54·3; H, 3·6%). All attempts to decompose the picrate by digesting with ammonia or sodium hydroxide were unsuccessful.

6 : 7-*Methylenedioxy*-3-(3′ : 4′-*dimethoxybenzyl*)-1 : 2 : 3 : 4-*tetrahydro*isoquinoline (XIII).—The substance (X) (4 g.) was suspended in 10% sulphuric acid (200 c.c.) and placed in an enamelled metal can, which constituted the cathode compartment of an electrolytic cell. The solution was heated to 90—95° and subjected to a current of 10 amperes, when the suspended sulphate gradually dissolved to a yellow solution which became colourless after 2 hours. The hot solution was filtered, made alkaline with strong ammonia, and extracted with chloroform; a red syrup remained on removing the solvent. This was extracted with boiling dilute hydrochloric acid, the solution filtered, and the filtrate treated with solid potassium iodide, when a sticky *hydriodide* separated which gradually hardened on cooling. This separated from alcohol, in which it was sparingly soluble, in small crystals, m. p. 226° (decomp.) (Found: C, 50·2; H, 5·0. $C_{19}H_{21}O_4N$,HI requires C, 50·1; H, 4·8%). The *hydrochloride*, obtained by digesting an aqueous solution of the hydriodide with silver chloride, crystallised from alcohol in small needles, m. p. 220—222° (decomp.). The *nitrosoamine* separated, on the addition of sodium nitrite to a solution of the hydrochloride, as an oil which hardened, and crystallised from alcohol in short needles, m. p. 128° (Found: C, 63·8; H, 5·7. $C_{19}H_{20}O_5N_2$ requires C, 64·0; H, 5·6%).

2 : 3-*Methylenedioxy*-11 : 12-*dimethoxy*-6 : 15 : 16 : 17-*tetrahydroparaberine* (IV).—The hydriodide of the base (XIII) (2 g.), dissolved

in methyl alcohol (10 c.c.), was decomposed with sodium bicarbonate and boiled for a few minutes with 40% formalin solution (10 c.c.). The mixture was cooled, diluted with water, sodium chloride added, and the solution decanted from the semi-solid mass which had separated. The latter was well washed with water, digested with concentrated hydrochloric acid (10 c.c.) on the steam-bath for a few minutes, diluted with water, and made alkaline with ammonia; an oil then separated which rapidly hardened. This was collected, triturated with methyl alcohol (15 c.c.), and the insoluble, colourless base (IV) (0·3 g.) collected and crystallised from benzene, from which it separated in small, colourless prisms, m. p. 221—222° (Found: C, 70·8; H, 6·4. $C_{20}H_{21}O_4N$ requires C, 70·8; H, 6·2%). The base (IV) is insoluble in water, sparingly soluble in ether, petroleum, or cold alcohol, moderately easily soluble in warm alcohol or benzene, and readily soluble in chloroform. The *hydrochloride* crystallises from water, in which it is fairly soluble, in small, colourless needles, m. p. 236—238°. The *picrate*, prepared in alcoholic solution, crystallises from alcohol in yellow nodules, m. p. 199—201° (decomp.) (Found: C, 54·5; H, 4·3. $C_{26}H_{24}O_{11}N_4$ requires C, 54·9; H, 4·2%). The *methiodide* was prepared by boiling a benzene solution of the base (IV) with an excess of methyl iodide for 1 hour, the solvent removed, and the residue crystallised from methyl alcohol, separating in large prisms, m. p. 268° (Found: C, 52·2; H, 5·2. $C_{21}H_{24}O_4NI$ requires C, 52·4; H, 5·0%). This methiodide was boiled with a large excess of 25% methyl-alcoholic potassium hydroxide for 6 hours, but, on cooling, crystals of the unchanged methiodide separated and no other substance could be isolated from the product. The methiodide was digested for 3 hours with an aqueous suspension of silver chloride and filtered, when the *methochloride* separated as a gelatinous precipitate, m. p. 260° (decomp.), from the filtrate. The methochloride was recovered after boiling for 6 hours with 25% methyl-alcoholic potassium hydroxide.

2 : 3-*Methylenedioxy*-11 : 12-*dimethoxy*-6 : 17 or -6 : 15-*dihydroparaberine* (XV or XVI).—The base (IV) (1 g.), dissolved in alcohol (20 c.c.) containing potassium acetate (1 g.), was treated with a 1% alcoholic solution of iodine (200 c.c.). After boiling for ½ hour, the mixture was cooled, and the crystalline periodide was collected and converted, by the action of sulphurous acid, into the bright yellow hydriodide; this was collected, boiled with water and the solution filtered hot. The residue consisted of a high-melting, orange-coloured hydriodide, the yield of which was too small to allow of detailed investigation. A small quantity, however, was converted into the hydrochloride by means of silver chloride, and this

gave an immediate precipitate with ammonia, showing that it was not a quaternary salt. The filtrate, on cooling, deposited pale yellow needles, m. p. 225—226° (Found: C, 51·5; H, 4·4. $C_{20}H_{19}O_4N$,HI requires C, 51·6; H, 4·3%). This *hydriodide* is sparingly soluble in cold water or cold alcohol, but moderately soluble in the warm solvents. The *hydrochloride* was obtained by digesting an aqueous solution of the hydriodide with silver chloride and separated from a little water in bright yellow needles which melted at 120° with loss of water of crystallisation. On drying at 120°, it lost 11·5% H_2O (Found: C, 63·3; H, 5·5. $C_{20}H_{19}O_4N$,HCl,$\frac{1}{2}H_2O$ requires C, 62·9; H, 5·5%). The *base* (XV or XVI) was obtained as a pale yellow, amorphous, gelatinous precipitate by the addition of ammonia to an aqueous solution of the hydrochloride, and was collected and dried. It was soluble in the usual organic solvents with the exception of petroleum, but it could not be obtained in the crystalline state. The addition of petroleum (b. p. 40—60°) to the dry ethereal solution precipitated the base as a pale yellow, amorphous powder melting indefinitely between 180° and 190° (Found: C, 70·9; H, 5·7. $C_{20}H_{19}O_4N$ requires C, 71·2; H, 5·6%).

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OXFORD. [*Received, November 21st*, 1925.]

X.—*Keto-enol Isomerism of Ethylenebisacetylacetone.*

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IN their reactions with inorganic reagents acetylacetone and its homologues exhibit the behaviour of three dynamic isomerides: (1) a diketonic form manifested in condensation with tellurium tetrachloride, (2) a *trans*-monoenolic form with selenium tetrachloride, and (3) a *cis*-monoenolic modification with copper acetate, ferric chloride and other metallic salts (Morgan and Drew, J., 1924, **125**, 1044).

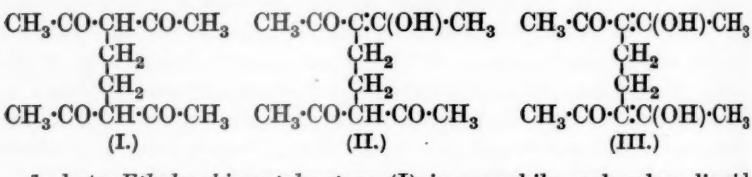
Ordinary acetylacetone consists principally of enolic forms and in 1921 K. Meyer and Hopff, by distilling the diketone under reduced pressure in silica vessels, succeeded in separating the

enolic and keto-forms, which, however, reverted rapidly to the equilibrium mixture (*Ber.*, 1921, **54**, 579).

With certain derivatives of acetylacetone the individual modifications are more stable. Thus Knoevenagel (*Ber.*, 1903, **36**, 2150) indicated two isomeric forms of methylenebisacetylacetone, one a solid and the other an oil, both of which developed deep violet colorations with ferric chloride. He regarded the oil as the dienolised form, since with ammonia it yielded diacetyldihydrolutidine, whereas the solid, which gave no dihydropyridine derivative with ammonia, he regarded as the monoenolised compound.

Schiff claimed to have isolated no fewer than six isomeric varieties of benzylidenebisacetylacetone, namely, a keto-form, two monoenols (*cis* and *trans*) and three dienols (di*cis*, di*trans* and *cis-trans*). He did not, however, characterise these various modifications (*Annalen*, 1899, **309**, 206).

In the present communication, ethylenebisacetylacetone, prepared by the condensation of sodium acetylacetone and ethylene dibromide, is shown to exist in at least three isomeric forms, which have been identified definitely as a keto-form (I), a monoenolic modification (II), and a dienolic variety (III).



(I.) (II.) (III.)

1. keto-*Ethylenebisacetylacetone* (I) is a mobile, colourless liquid of high boiling point; its alcoholic solution only slowly develops a violet colour with ferric chloride.

2. monoenol-*Ethylenebisacetylacetone* (II) is obtained in prismatic crystals, m. p. 99°; its alcoholic solution develops instantaneously a deep violet coloration with ferric chloride.

3. dienol-*Ethylenebisacetylacetone* (III) separates in cubical crystals, m. p. 140—143°, and reacts immediately with ferric chloride. This form is, however, less stable in air than the preceding varieties and the melting point of the crystals soon falls to about 100—110°.

The foregoing isomerides were characterised by an application of Meyer's method for estimating the percentage of enolic modification in a tautomeric substance such as acetylacetone (*Annalen*, 1911, **380**, 212; 1913, **398**, 49; *Ber.*, 1911, **44**, 2718; 1912, **45**, 2843), which depends on the rapid addition of bromine to the enolic modification, but not to the ketonic form. When treated with excess of hydroxylamine, *keto*-ethylenebisacetylacetone and *enol*-

ethylenebisacetylacetone both yield stereoisomeric tetraoximes. In the latter oximation, it is evident that hydroxylamine causes the enolic modification to revert to the ketonic isomeride.

EXPERIMENTAL.

Interaction of Sodium Acetylacetone and Ethylene Dibromide.—Sodium acetylacetone (210 g.) was mixed with excess of ethylene dibromide (600 g.) and refluxed at 160° for 12 hours; the mixture was then allowed to cool and the deposit of sodium bromide washed with ether. The weight of bromide corresponded nearly quantitatively with the amount of sodium originally in the sodium acetylacetone.

The brown ethereal filtrates were distilled, ether and ethylene dibromide being collected up to 135° and acetylacetone from 135° to 145°; the residue was transferred to a Claisen flask and distilled under reduced pressure (3—5 mm.), and the following fractions were collected: (1) b. p. 60—80°—contained the remainder of the ethylene dibromide and acetylacetone; (2) b. p. 80—100°—25 g. of a slightly yellow liquid boiling under ordinary pressure at about 200°. Its alcoholic solution gave no immediate coloration with ferric chloride, but a violet coloration slowly developed; it did not give a copper salt with ammoniacal copper acetate; (3) b. p. 120—130°—8·5 g. of a yellow oil; its alcoholic solution gave an immediate violet colour with ferric chloride and a small precipitate of copper salt with ammoniacal cupric acetate; (4) b. p. 170—200°—19 g. of a brown, viscid oil which gave an instantaneous ferric coloration and a copious precipitate with ammoniacal cupric acetate.

I. keto-*Ethylenebisacetylacetone* (I).—The principal product of the reaction, represented by the second fraction (b. p. 80—100°), was redistilled under reduced pressure, when about 80% distilled between 83° and 85°/4 mm. The resultant liquid was slightly yellow, readily miscible with water, alcohol, benzene, ether, or chloroform, but not with light petroleum; it dissolved in dilute sodium hydroxide to a yellow solution. A sodium salt was formed by adding metallic sodium to the liquid dissolved in ether.

After several distillations under reduced pressure, keto-*ethylenebisacetylacetone* boiled at 97—99°/20 mm. (Found: C, 63·3, 63·9; H, 7·9, 7·9. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%).

II. *Dehydration Product of Ethylenebisacetylacetone.*—The third fraction (b. p. 120—130°) did not solidify on keeping in the ice chest and was therefore dissolved in alcohol and treated with an excess of ammoniacal cupric acetate, when on dilution with water a small amount of copper salt was precipitated, but the major part of the substance evidently remained dissolved in the aqueous-

alcoholic filtrate. By diluting further with water and extracting several times with ether, a light brown oil was obtained, which soon crystallised. After repeated crystallisation from alcohol, the substance separated in colourless, hexagonal plates or laminæ, but only a very small amount was isolated. Its alcoholic solution did not respond to ferric chloride (Found : C, 72·2, 72·4; H, 8·2, 7·3. $C_{24}H_{30}O_5$ requires C, 72·4; H, 7·5%, thus corresponding with a possible dehydration product of ethylenebisacetylacetone : $2C_{12}H_{18}O_4 - 3H_2O = C_{24}H_{30}O_5$) (Knoevenagel, *loc. cit.*).

III. enol-*Ethylenebisacetylacetone* (II).—The fourth fraction (b. p. 170—200°) was cooled in ice, when crystallisation set in. The first deposit consisted of a mass of needles which, after washing with a little ether, were colourless and melted at 134°. Recrystallisation from alcohol or benzene gave a product with indefinite melting point, liquefaction commencing at about 100°, but not being complete until 130°. Its alcoholic solution gave an intense violet colour with ferric chloride and a copper derivative with ammoniacal cupric acetate.

When left in the ice chest for several days, the mother-liquors deposited prismatic crystals; these, when washed free from oil with the aid of ether, melted at 98—99°. Recrystallisation from benzene gave a mass of glistening, white needles, m. p. 99—100°; recrystallisation from alcohol also gave very fine needles melting at 99°. A mixture of the original crystals with those obtained after recrystallisation from alcohol and from benzene also melted at 98°, which indicated a definite substance and not a mixture (Found : C, 63·6, 63·7; H, 8·0, 8·2. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%).

This monoenol-*ethylenebisacetylacetone* (p. 44) when dissolved in alcohol gave an instantaneous deep violet coloration with ferric chloride and a precipitate of a copper salt with ammoniacal cupric acetate. After keeping for some months, its melting point became 146—152°.

IV. dienol-*Ethylenebisacetylacetone* (III). — The mother-liquors from the crystals of the monoenol showed no further signs of crystallisation and were converted into the copper derivative by treating an alcoholic solution with excess of ammoniacal cupric acetate. After drying, the mass was extracted with benzene; a faintly yellow solution was obtained which on evaporation of the solvent left a few drops of a brown oil, whilst the copper salt remained as an insoluble greenish-grey powder. It had no definite melting point, but decomposed above 250°, and was quite insoluble in all organic solvents. It contained 18% of copper. $C_{24}H_{34}O_8Cu$ requires Cu, 12·3 and $C_{12}H_{16}O_4Cu$ requires Cu, 22·1%.

The copper salt was decomposed with sulphuric acid in the presence of ether; a white precipitate was formed and was filtered off, whilst the ethereal layer was allowed to evaporate. The insoluble product with indefinite melting point of 100—107° was subsequently shown to be a mixture of mono- and di-enolic forms. The product separating from the ethereal layer formed colourless, cubic crystals which after washing with ether melted more definitely at 140—143° and consisted chiefly of dienol-*ethylenebisacetylacetone* (Found: C, 63·6; H, 7·9. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%).

When kept for some time, the melting point of the dienol became indefinite; melting commenced at 100°, but was not complete until about 140°. This change in fusibility probably indicated a partial transformation into a mixture of the mono- and di-enolic forms.

V. *Comparative Study of the Behaviour of the Three Isomerides towards Bromine.*—A known weight of the isomeride under investigation, dissolved in sufficient alcohol to give an approximately *M*/20-solution, was treated with *N*/10-bromine (alcoholic) in the cold until the yellow colour persisted; an alcoholic solution of β-naphthol was then quickly added to absorb the excess of bromine. Potassium iodide was added and the solution gently warmed; iodine was liberated and titrated by means of *N*/10-thiosulphate without the use of an indicator, 1 g.-mol. of iodine being equivalent to one double bond, that is, to one hydroxyl group.

(*a*) *The liquid* keto-*ethylenebisacetylacetone*: 1 g.-mol. liberates 0·033 × 127 g. of iodine, corresponding with the presence of about 0·8% of the enolic form.

(*b*) enol-*Ethylenebisacetylacetone*, m. p. 98—99°: 1 g.-mol. liberates 2 × 127 g. of iodine, corresponding with the pure monoenolic form of ethylenebisacetylatetone.

(*c*) dienol-*Ethylenebisacetylacetone*, m. p. 140—143°: 1 g.-mol. liberates 2·5 × 127 g. of iodine; this indicates the presence of about 1·25 hydroxyl groups per g.-mol. or a mixture of 25% of the dienolic with 75% of the monoenolic form of ethylenebisacetylacetone.

From these results, we conclude that in the case of the liquid and the solid, m. p. 98°, we are dealing with the comparatively stable ketonic and monoenolic forms of ethylenebisacetylacetone, respectively. The other product, m. p. 140—143°, may be an equilibrium mixture; or more probably it represents in the solid state the true dienolic form, which in alcoholic solution becomes transformed into an equilibrium mixture.

Comparative Study of the Ketonic and Monoenolic Forms of Ethylenebisacetylacetone.—Stereoisomeric tetraoximes. The liquid *keto*-ethylenebisacetylacetone and the solid enol modification were each heated on the water-bath for 2 hours in dilute alcohol with

excess of hydroxylamine hydrochloride (6—8 mols.) and sodium acetate. On the mixture being poured into water, the *α-tetraoxime* from the keto-form remained in solution, and was extracted with ether. It separated from the concentrated ethereal extract in colourless crystals, m. p. 165° (Found: N, 19·15. $C_{12}H_{22}O_4N_4$ requires N, 19·6%).

The *β-tetraoxime* from the enol form separated as a white solid crystallisable from hot water in minute, colourless needles decomposing at 220—222° (Found: N, 19·7%).

Tellurium Tetrachloride and keto-*Ethylenebisacetylacetone.*—The liquid keto-form (9 g. = 2 mols.) and 5·4 g. (1 mol.) of tellurium tetrachloride were refluxed in chloroform solution. The mixture immediately blackened, but little or no hydrogen chloride was evolved until after ½ hour; the gas was then freely evolved during 3 hours. The filtrate from tellurium (0·4 g.) was concentrated in a vacuum desiccator. A black tar remained; no crystallisation took place even after one month or on treatment with various solvents. On extraction with *n*-hexane, the tar remained undissolved, but after evaporaton of the hydrocarbon crystalline laminæ were left. By pressing these on a porous plate, white crystals were obtained, which were purified by crystallisation from hexane. Hexagonal prisms resulted, m. p. 79°, yield 1 g. The product was readily soluble in alcohol and the solution gave an immediate intense purple colour with ferric chloride; it also yielded a copper salt. Qualitative tests showed the absence of tellurium, but chlorine was present and could be detached by boiling with aqueous potash (Found: C, 52·0, 51·6; H, 7·0, 6·9. $C_7H_{11}O_2Cl$ requires C, 51·7; H, 6·8%). This analysis corresponds with a removal of one acetylacetone residue and the formation of β-chloroethylacetylacetone, $CH_2Cl{\cdot}CH_2{\cdot}CH(CO{\cdot}CH_3)_2$.

Transformations of enol-*Ethylenebisacetylacetone into its Isomerides.*—*Ketonisation.* The monoenol formed stable, prismatic crystals, m. p. 99°. It was slightly soluble in water and the solution reacted faintly acid to litmus. It readily dissolved in dilute caustic soda to a yellow solution of the sodium salt; no precipitate was produced when this solution was acidified with sulphuric acid in the cold, and extraction with ether yielded an oil which failed to colour ferric chloride and was probably the ketonic form.

Dienolisation. The copper salt, prepared from the monoenolic form by treating a solution in alcohol with excess of ammoniacal cupric acetate, dried to an amorphous, greenish-grey powder quite insoluble in all organic solvents, thus differing from the usual co-ordinated copper derivatives obtained from the β-diketones. It contained 19·3% of copper; the amount calculated for the copper

derivative of the monoenol is 12·3, and for that of the dienol 22·1%. When decomposed in the usual manner with sulphuric acid in the presence of ether, an amorphous, white solid is precipitated which is only sparingly soluble in ether; after washing with ether and drying, this melts at 98° and is the monoenolic form, but the substance which crystallises from the ethereal solution has an indefinite melting point; it softens and loses its crystalline form at 110°, but does not run down the tube to a clear liquid until 130—134°, behaving as a mixture of the di- and mono-enolic forms; Meyer's test indicates the presence of about 20% of the dienolic form with 80% of the monoenolic. It is evident that under the influence of ammoniacal cupric acetate the monoenol changes partly to the dienol.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research and to the Government Grant Committee of the Royal Society for grants which have helped to defray the expense of this investigation.

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EDGBASTON. [*Received, November 17th*, 1925.]

XI.—*The Solubilities of Sodium, Potassium, and Calcium Ferrocyanides. Part I.*

By MONICA FARROW.

THIS investigation was undertaken on account of the uncertainty of the solubility data for the ferrocyanides of sodium and potassium, and the lack of data for the calcium salt. Early workers, *e.g.*, Michel and Kraft (*Ann. Chim. Phys.*, 1854, **41**, 482), Étard (*ibid.*, 1894, **2**, 546), and Schiff (*Annalen*, 1860, **113**, 350), obtained values varying from 25 to 40 g. of potassium ferrocyanide in 100 g. of water at 20°. Determinations for the potassium and sodium salts were made at a few temperatures by Conroy (*J. Soc. Chem. Ind.*, 1898, **17**, 104), by Harkins and Pearce (*J. Amer. Chem. Soc.*, 1916, **38**, 2716) at 25° only, by Fabria (*Gazzetta*, 1921, **51**, ii, 374) over the whole range from the cryohydric point to 100°, and by Vallance (*Chem. News*, 1922, **125**, 7) for the potassium salt only, at low temperatures.

Purification of the Salts.—The purest sodium and potassium ferrocyanides obtainable were further purified by rapid crystallisation from hot water. By simple qualitative tests the absence of the most likely impurities, calcium and ammonium, was proved.

The purest calcium salt obtainable, for which we are indebted

to Mr. W. G. Adam of the Gas Light & Coke Co., was slightly tinged with blue. It was purified by precipitation with absolute alcohol in the cold (to avoid oxidation) from an air-free saturated solution. The pure lemon-yellow, finely crystalline product was centrifuged, dried in vacuum desiccators, first over charcoal for 24 hours, then over the partly dehydrated salt, and stored in the dark in dark glass-stoppered bottles. No discoloration appeared after 18 months. No trace of sodium, potassium, or ammonium could be detected in the residue left after decomposition of the salt with concentrated sulphuric acid. Determinations of calcium as oxalate in the original and the purified salt proved that no measurable change of composition had resulted from the purification process:

Orig. salt: 16·2, 16·2, 16·2, 16·3, 16·25, 16·1, 16·2, 16·2. Mean, 16·2% Ca.

Recryst. salt: 16·2, 16·25, 16·2, 16·2, 16·2, 16·2, 16·2, 16·3. Mean, 16·2% Ca.

There has been some doubt about the precise number of molecules of water in the calcium salt. The above determinations, which lie much nearer to the theoretical value for a hydration of $11H_2O$ (16·3% Ca) than to that for $12H_2O$ (15·8% Ca), support the conclusion of Berkeley, Hartley, and Burton (*Phil. Trans.*, 1908, **209***A*, 177) that the lower figure is correct. The lower figure is also in accordance with the recent careful determinations of Cumming (J., 1924, **125**, 240).

Method of Determining Solubility.—A solution was heated in contact with excess of the solute to the required temperature and after the attainment of equilibrium a definite volume was withdrawn in a weight pipette to be weighed and analysed, and the density calculated.

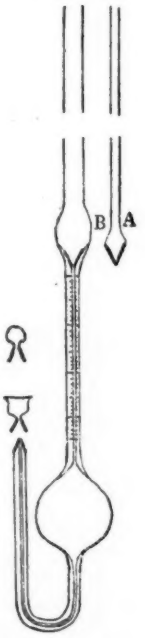
The ferrocyanide in all three salts was estimated volumetrically with permanganate by the simple method of de Haen (Treadwell, "Quantitative Analysis," p. 632). This method after practice gave concordant results; it is essential to standardise the solution used against standard potassium ferrocyanide and not against the customary oxalic acid. The calcium ferrocyanide was also determined independently as oxalate.

Cumming's method of estimating ferrocyanides with benzidine hydrochloride (J., 1924, **125**, 240) was tried, but it did not appear so suitable for these metallic ferrocyanides as the simple permanganate method and was therefore not employed.

Pure dilute boiling sodium oxalate solution was used in the determination of the calcium salt as oxalate, because ammonium oxalate and oxalic acid as precipitants produced insoluble double calcium

ammonium ferrocyanide and insoluble hydroferrocyanic acid, respectively. In the first experiments, in which an alundum cone was used as a filter, no sharp end-point could be obtained on the addition of permanganate, owing to slow diffusion of oxalate from the inner pores of the cone. Gooch crucibles were substituted for the cones, but even then the permanganate readings were not concordant. The asbestos used had no reducing action on permanganate, and experiment also showed that no measurable occlusion occurred at the dilutions used. The cause of the error was traced to the appreciable solubility of calcium oxalate in water. The washing was therefore limited to three fillings of the Gooch, and this procedure was kept constant throughout the experiments.

FIG. 1.



Apparatus.—The solubility vessel consisted of a wide tube of about 200 c.c. capacity, fitted with a rubber bung and stirrer. In order to hold the pipette in place in the solubility vessel the bung carried a short glass tube which was closed when not in use. The temperature of the thermostat was constant to within 0·2°.

The weight pipette, which had a volume of about 4·5 c.c. (Fig. 1), was of a design which has been used for several investigations in this laboratory, but has not previously been described. It is warmed to the temperature of experiment and introduced into the solution with its shorter arm fitted with a glass-wool filter adapted to the ground end. The solution can then be admitted by opening the ground-in plug, A; when it has reached the required level, which can be accurately read by means of the graduations, the plug is replaced. The pipette is then removed, the filter immediately replaced by a ground-on cap, and the whole cleaned and weighed after attaining room temperature. The pipette was repeatedly calibrated with pure mercury to give accurate volume readings for the density determinations.

Owing to the high solubilities of the calcium salt, these solutions were very viscous and consequently difficult to introduce into the pipette. To hasten the filling, slight pressure was applied to the solution in the solubility vessel. The determinations of solubility and density were in almost every case repeated at least once, and, as the data of the table show, the individual solubility experiments very seldom differed from the mean by more than 0·1 unit, or the densities by more than 0·002, except at the highest temperatures,

when the experimental difficulties already mentioned make the determinations somewhat less concordant.

Solubilities and Densities.

g = grams of anhydrous salt in 100 grams of solution. d = density of saturated solutions. The mean values are printed in italics.

	$K_4Fe(CN)_6$.		$Na_4Fe(CN)_6$.		$Ca_2Fe(CN)_6$.	
Temp.	*g.*	*d.*	*g.*	*d.*	*g.*	*d.*
24·9°	23·96	1·1731	17·10	1·1330	36·52	1·3574
	23·83	1·1731	17·15	1·1295	36·42	1·3552
	24·00	1·1734	17·08	1·1312	36·45*	*1·3563*
	24·01	1·1729	*17·11*	*1·1312*	36·36*	
	23·95	*1·1731*			*36·44*	
34·9	28·00	1·2026	20·58	1·1576	39·11	1·3633
	28·08	1·2014	20·58	1·1591	39·30	1·3690
	27·95	1·2015	*20·58*	*1·1584*	39·09*	*1·3662*
	28·01	*1·2018*			39·38*	
					39·22	
49·8	33·26	1·2360	26·16	1·2009	41·98	1·3975
	33·00	1·2340	26·23	1·2000	41·99	1·3964
	33·13	*1·2350*	*26·20*	*1·2004*	42·12*	*1·3970*
					42·06*	
					42·04	
64·7	37·05	1·2627	31·45	1·2432	44·28	1·4071
	36·83	1·2644	31·41	1·2421	44·27	1·4077
	36·94	*1·2635*	*31·43*	*1·2426*	44·72*	*1·4074*
					44·48*	
					44·44	
79·6	40·36	1·2858	36·87	1·2794		
	40·54	1·2850	36·83	1·2779		
	40·45	*1·2854*	*36·85*	*1·2786*		
84·7			37·96	1·2891		
			38·33	1·2942		
			38·15	*1·2916*		
89·6			38·08	1·2959		
94·7			38·25	1·2870		
99·7	43·83	1·3148	37·45	1·2928		
	43·72	1·3082	37·55	1·2849		
	43·78	*1·3115*	37·55	1·2806		
			37·65	*1·2861*		
			37·47			
			37·53			

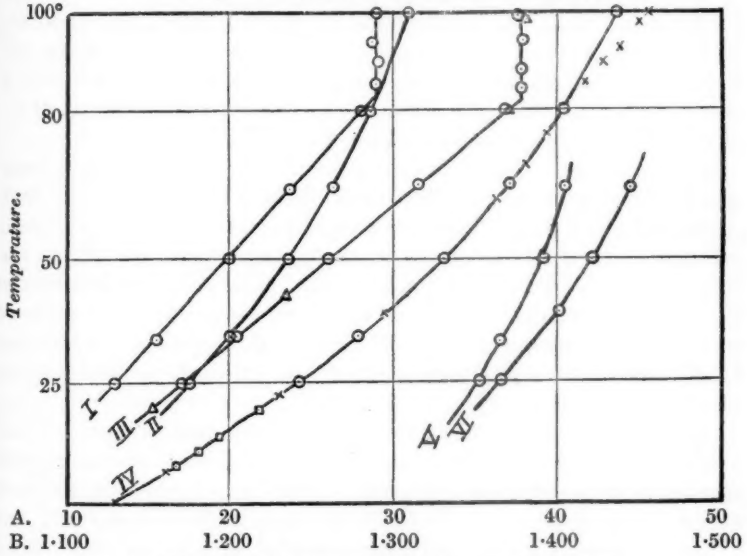
* As oxalate, the rest as ferrocyanide.

Results of Experiments.—The values obtained for the solubilities of calcium and potassium ferrocyanide lie on two smooth curves (Fig. 2). The values obtained by Vallance and by Fabria (*loc. cit.*) for the potassium salt, which are plotted on our curve for purposes of comparison, are in good agreement with our measurements except at temperatures above 84°, where Fabria's values are considerably higher. To what extent the divergence is due to his having kept his solutions at these high temperatures for as long as 3 hours we are unable to say, but we have repeatedly noticed that solutions of the calcium salt show green coloration on

cooling, owing presumably to incipient decomposition. The experimental difficulties with the calcium salt solutions at high temperatures were considerable. The solutions had both high viscosity and high density; the former made the rate of flow into the pipette very slow, and also prevented the very small particles of solid salt from settling rapidly. It was almost impossible to prevent the capillary entrance to the pipette from being blocked, and although five determinations were made for the solubility at

FIG. 2.

△ *Conroy.* ⊡ *Vallance.* × *Fabria.* ⊙ *Authors.*



A. *Grams of anhydrous salt in* 100 *grams of solution.*
B. *Density of saturated solution.*

I. *Density of sodium ferrocyanide solutions.* II. *Density of potassium ferrocyanide solutions.* III. *Solubility of sodium ferrocyanide.* IV. *Solubility of potassium ferrocyanide.* V. *Density of calcium ferrocyanide solutions.* VI. *Solubility of calcium ferrocyanide.*

79·6° these are not given, as they show almost the same value as that obtained at 65°.

As may be seen from the graph, the solubility curve of sodium ferrocyanide shows a sharp break at 81·7°. This transition temperature does not appear to have been observed before, though it is apparently responsible for the reported transition in the curve for the potassium salt of Étard (*loc. cit.*). Work is in progress on the three-component system calcium ferrocyanide–sodium ferrocyanide–water, and the identity of the lower hydrate of the sodium

salt will be investigated. The four points given by Conroy (*loc. cit.*) for the solubility of the sodium salt lie almost exactly on our curve, though, as the number of his determinations was small, the transition point evidently escaped his observation. The density results (Fig. 2) require little comment. No other work appears to have been done on this property of the saturated solutions. The three curves are of the same general form as the corresponding solubility ones. In the case of the sodium salt, the points evidently lie on two curves and are consistent with the transition at 81·7° as given by the solubility curve.

Verification of the Transition Temperature of Sodium Ferrocyanide.—The transition point was verified by the two following methods:

1. *The cooling curve.* On allowing the salt to cool from about 90° to 75° in a jacketed test-tube carrying a copper stirrer and a sensitive thermometer, arrests were observed, in three experiments, at 81·0°, 81·2°, 81·3°, giving a mean value of 81·2°.

2. *Dilatometer.* The dilatometer used was of the ordinary form and had a graduated capillary neck about a foot long. The bulb contained the hydrate ($10H_2O$) and sufficient paraffin to rise to a convenient level in the capillary when the temperature was in the region of 81°. Before the dilatometer was introduced into the thermostat it was heated above 81° so as always to have some of the higher-temperature hydrate present to facilitate the change. In all, six experiments were carried out at temperatures ranging from 80·6° to 82·6°.

At the highest temperature, 82·6°, there was a rapid rise of 1 inch in nearly 3 minutes, and at 81·9° the level of the oil still rose, although at the rate of only $\frac{1}{2}$ inch in $\frac{1}{2}$ hour. In the next three determinations at 81·2°, 81·3°, and 81·3°, respectively, no change in the oil level could be observed. Finally, at 80·6°, there was a fall in the level of $\frac{1}{2}$ inch in $\frac{1}{4}$ hour. These experiments show that the change from the higher-temperature hydrate to the $10H_2O$-hydrate occurs with a volume decrease and vice versa, and that the most probable value of the transition temperature is 81·5°. The values obtained by the less accurate methods, namely, 81·7° by the solubility, and 81·2° by cooling curves, give as a mean value one very close to the most trustworthy value of 81·5°.

Summary.

1. The solubility of sodium, potassium, and calcium ferrocyanide in water has been determined, together with the density of the saturated solutions.

2. Sodium ferrocyanide has a transition point at 81·5°. Neither the potassium nor the calcium salt shows any transition over the

range investigated, the transition point of the potassium salt recorded by Étard being probably due to contamination with sodium ferrocyanide.

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XII.—*Studies of Valency. Part VII. Surface Polarity and the Reaction of Ethylene and Chlorine—The Effect of the Adsorbed Water Layer.*

By RONALD GEORGE WREYFORD NORRISH and GRIFFITH GLYN JONES.

THE reaction between ethylene and bromine which occurs only at the surface of the reaction vessel (Stewart and Edlund, *J. Amer. Chem. Soc.*, 1923, **45**, 1014) has been shown by one of us to depend greatly on the nature of the surface (Norrish, J., 1923, **123**, 3006). The following figures represent the mean bimolecular velocity coefficients found for the surfaces specified in vessels of uniform dimensions: Glass, 0·0506; stearic acid, 0·0864; cetyl alcohol, 0·0266; paraffin wax, 0·0030. The low value for paraffin wax suggested that these figures might be taken as a measure of the polarity of the surfaces and that with an improvement in technique the method might be used as a general measure of surface polarity.

The present research has been undertaken to investigate the effect of moisture on the reactivity of glass and paraffin surfaces and to test a suggestion put forward in the previous paper on ethylene and bromine (*loc. cit.*), that the absolute reactivity of a paraffin surface is vanishingly small.

In these experiments we have substituted chlorine for bromine since it is more easily manipulated than the latter and admits of the pressures of the reactants being increased tenfold. Furthermore, an easier means of experimentation, which gives accurate and reproducible results, has been devised. As was expected, in view of the previous results, the reaction between ethylene and chlorine (in the absence of light) has been found to occur entirely at the surface, and to depend on the nature of the surface in the same way as the reaction of ethylene and bromine already studied. It has further been shown that whilst the rate of reaction at a paraffin wax surface is independent of the presence of water vapour, this is not so for a glass surface, the gases, in the presence of water vapour at 6 mm. pressure, uniting 1·3 times as fast as when they were dried

by phosphoric acid. Further, by taking special precautions to prevent accidental exposure of the glass, it was found possible practically to suspend the reaction in a paraffin vessel, less than 0·1 of the total reactants combining in the course of 12 hours, whilst, in the case of a glass vessel of the same dimensions, the reaction was practically complete in 30—40 minutes. This indicates a reactivity for a paraffin surface some 1200 times smaller than for a glass surface of the same dimensions, whereas the earlier ethylene-bromine experiments indicated a reactivity for paraffin wax only 18 times smaller than that for glass.

FIG. 1.

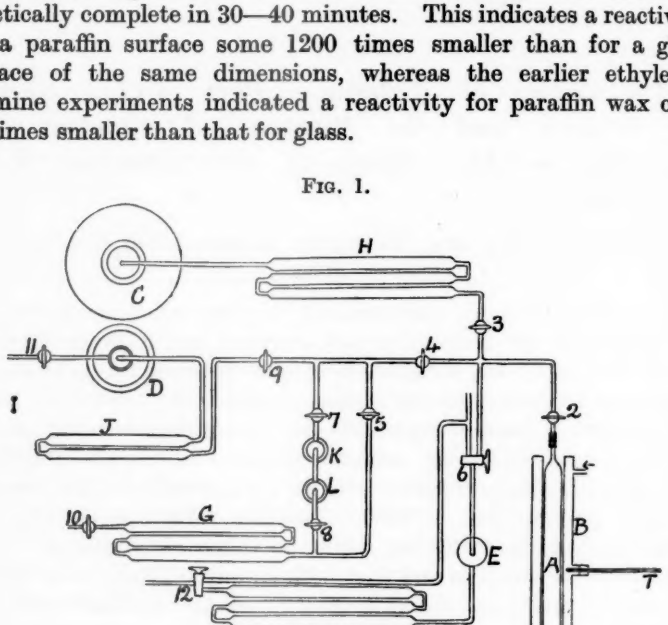


FIG. 2.

EXPERIMENTAL.

The reaction vessel (Fig. 1, A) consisted of a glass tube 35 cm. long and either 1·3 or 2·7 cm. in diameter. The tube was water-jacketed by an outer metal vessel, B, which served to screen it from light and was kept at constant temperature by a current of water circulated by a pump from a thermostat regulated to 0·1°, the temperature being indicated by a thermometer T. One end of the reaction vessel was connected *via* tap 1 and a long capillary tube to a vertical mercury manometer M; the other end was connected *via* tap 2 to the gas supply and water-pump. As it was necessary frequently to remove the reaction vessel, its connexion with taps 1 and 2 was made at first by paraffined rubber pressure tubing and

later by ground glass joints. The apparatus could be evacuated *via* taps 2, 4, 9, 11, by way of the drying tubes, J, containing phosphoric oxide, and the expansion chamber, D, containing calcium chloride. Dry air could be admitted *via* the drying tubes, G, containing calcium chloride and phosphoric oxide, by way of taps 10, 5, 4, 2. Air saturated with water vapour could be admitted by way of the saturators L and K and taps 10, 8, 7, 4, 2. The saturators were so arranged that the air bubbled through the liquid in L and passed over the surface of the liquid in K. Ethylene was stored in the aspirator, C, and could be expanded into the reaction vessel by way of the calcium chloride–phosphoric oxide drying system, and taps 3 and 2. Dry chlorine was obtained *via* taps 6 and 2 from the chlorine chamber, E, which was kept continually filled by the passage of chlorine from a cylinder, through the phosphoric oxide drying system, F. The technique of the chlorine manipulation was similar to that already described by Norrish and Rideal (J., 1925, **127**, 787).

An experimental run was carried out as follows. The vessel A was evacuated as far as possible by the water-pump, and washed out with dry air and re-evacuated several times. Finally air, either dry or moist as required, was admitted to a pressure of about 300 mm. The connecting tubes were evacuated and washed out two or three times with ethylene, and then dry ethlyene was admitted to the reaction vessel to a partial pressure of 200 mm. Finally, after the connecting tubes had been washed out as before, dry chlorine was admitted to a partial pressure of 200 mm. Stop-cocks 1 and 2 were kept closed throughout the reaction and readings of the pressure were made at intervals by momentarily putting the mercury manometer into communication with A by opening tap 1; when these precautions were taken, the mercury of the manometer was not affected by the chlorine if this gas was the last to be admitted to the system.

The bimolecular reaction coefficient used as a measure of the reactivity of a given surface was calculated by the formula

$$k = x/a(a - x)t,$$

where a is the initial pressure of ethylene or chlorine, and x the fall in pressure of either gas at time t. The value of a was fixed at 200 mm., and the value of x calculated from the fall of pressure in the reaction chamber, account being taken of the fact that the ethylene dichloride is initally formed as a gas and finally separates as a liquid when its saturation vapour pressure is reached. This vapour pressure is 55 mm. at 18°, and 60 mm. at 20° (Rex, *Z. physikal. Chem.*, 1906, **35**, 358); hence if dp represents the pressure fall at time t at 20°, then, when $dp < 60$ mm., $x = dp$, and when

$dp > 60$ mm., $x = (dp + 60)/2$. There was, in general, no noticeable change in the value of k at the moment when liquid ethylene dichloride separated, a fact which proves that the liquid exerts no appreciable catalytic activity in the reaction.

For a reaction which occurs solely at the surface, as in the present case, it may be shown that the reaction coefficient, calculated as above in terms of pressure changes, must be multiplied by the factor v/s, representing the ratio of volume to surface of the reaction vessel, in order to obtain comparable figures for different-sized vessels. In the present experiments, cylindrical tubes of uniform length were used as the reaction vessels, for which $v/s \propto d$, where d is the diameter of the tube. Thus, by taking the product kd we obtain comparable figures for surface reactivity. In Tables I and IV examples are given in full of various experiments. The further account of this work will be limited to giving figures for surface reactivity, in Tables II and III, calculated as described above from the mean reaction velocity coefficients.

TABLE I.

Effect of water vapour on the reaction of ethylene and chlorine at a glass surface.

Diameter of tube, 1·30 cm. Temp., 18°.

Experiment "Glass 10." a, 200 mm. Water vap. press., 0.			Experiment "Glass 11." a, 202 mm. Water vap. press., 6·2 mm.		
Time (mins.).	Total pressure fall (mm.).	$k \times 10^4$.	Time (mins.).	Total pressure fall (mm.).	$k \times 10^4$.
0	0	—	0	0	—
2	49	8·1	2	69	11·0
4	95	7·5	4	131	10·6
6	129	7·1	6	174	10·8
8	159	7·4	8	204	11·1
10	181·5	7·2	10	224·5	11·0
12	199	7·3	12	239·5	11·1
15	220	7·3	14	251	11·1
18	234	7·2	16	261·5	11·2
21	245·5	7·3	18	267	10·8
25	256·5	7·0	21	276	10·6
30	266·5	6·8	25	284	10·3
		Mean 7·3			Mean 10·9
Surface reactivity (kd) = $9·5 \times 10^{-4}$.			Surface reactivity (kd) = $14·2 \times 10^{-4}$.		

From the data of Table II, which are given in the order of experimentation, it will be seen that the surface reactivity, kd, is uniformly higher for moist gases than for dry, the mean value, calculated from the recorded figures, being $11·3 \times 10^{-4}$ for dry gases and $14·8 \times 10^{-4}$ for moist gases, while the ranges of surface reactivity in the two cases do not overlap. Thus the presence of about 6 mm. of

TABLE II.

Effect of water vapour on the reaction of ethylene and chlorine at a glass surface—collected data.

Diameter of tube, 1·30 cm.

Expt. No.	Temp.	Water vapour pressure.	Bimolec. reaction coeff. $k \times 10^4$.	Surface reactivity. $kd \times 10^4$.
2	18°	0	8·2	10·7
4	19	0	7·9	10·3
5	18	6·0	11·0	14·3
6	19	6·6	11·7	15·2
7	19	0	9·6	12·5
9	16	5·1	11·6	15·1
10	18	0	7·3	9·5
11	18	6·2	10·9	14·2
12	18	5·5	12·0	15·6
13	18	0	10·0	13·0
14	18	0	9·0	11·7
15	18	0	8·9	11·6
16	18	6·2	11·0	14·3

TABLE III.

Effect of water vapour on the reaction of ethylene and chlorine in a paraffin wax tube (rubber connexions).

Temperature, 20°.

Tube. No.	Diam. of tube (cm.).	Press. of water vapour (mm. Hg).	Vel. coeff. $k \times 10^4$.	Surface reactivity. $kd \times 10^4$.
1	1·3	6	0·74	0·97
		0	0·65	0·85
		0	0·71	0·92
2	2·7	6	0·17	0·45
		0	0·17	0·47
3	2·7	0	0·13	0·37
		6	0·12	0·33

water vapour in the gas phase increases the reactivity of a glass surface by about 30%.

It will be seen from the data for a given tube that the presence of water vapour has no measurable effect upon the reactivity of a paraffin wax surface. Further, the velocity coefficient does not vary in inverse ratio to the diameter of the tube as it would if the reactivities of the paraffin surfaces were uniform, and it was therefore thought that the measured reactivity was to be ascribed in part at least to the presence of the rubber connexions. In order to measure the absolute reactivity of a paraffin wax surface, the rubber connexions were replaced by ground glass joints, which together with the stop-cocks were lubricated with a grease made by melting together "nujol" and paraffin wax. The tube was constructed as shown in Fig. 2; the gases being introduced through the end A, and the end B being attached to the manometer. The paraffin

wax was introduced molten into the tube, and allowed to cool with constant agitation under a vacuum, the process usually having to be repeated several times before a uniform coat was obtained. The tube fitting the ground glass joint, and communicating with the manometer, was paraffined carefully on both sides of the tap C. Great difficulty was experienced in preparing satisfactory tubes; in most cases there was some small surface of glass incompletely protected which enabled a slow reaction to proceed. After many trials, however, two cases of very low reactivity were obtained. In the better of the two, with both reactants at *ca.* 200 mm. pressure, less than 0·1 of the total reaction had occurred after 12 hours. The experimental figures are in Table IV.

TABLE IV.

Tube dimensions: length, 35 cm.; diameter, 1·3 cm.

Experiment i. Temp., 20·4°. Pressure of C_2H_4, 197 mm. Press. of Cl_2, 200 mm.			Experiment ii. Temp. 20·0°. Pressure of C_2H_4, 220 mm. Pressure of Cl_2, 182 mm.		
Time (mins).	Pressure decrease (mm.).	Bimolec. coeff. × 10^6.	Time (mins.)	Pressure decrease (mm.).	Bimolec. coeff. × 10^6.
0	0	—	0	0	—
16·5	3·5	5·5	124	3·9	0·88
46	8·2	4·8	227	5·5	0·64
146	18·0	3·5	358	7·0	0·53
194	21·0	3·2	449	11·0	0·65
226	25·0	3·3	825	20·0	0·60
339	35·6	3·3	955	24·4	0·72
455	45·4	3·3	1096	32·5	0·89
525	52·0	3·7	1182	42·0	0·95

To ascertain that the gases remained unreacted in the tube, in experiment ii, they were slowly withdrawn, after 20 hours, through potassium iodide solution. The quantity of unreacted chlorine (estimated by the amount of iodine set free, equiv. to 7·20 c.c. of 0·1*N*-$Na_2S_2O_3$) was in satisfactory agreement (5%) with that (7·56 c.c.) calculated from the known volume of the tube (48 c.c.) and the observed pressure changes.

The reactivity of the tube in experiment ii was much lower than that in experiment i, a fact which suggests that this residual activity was entirely due to the accidental exposure of glass surface.

Reactivity of a Stearic Acid Surface.—As data for comparison with the experimental results of the ethylene–bromine reaction (*loc. cit.*), figures were obtained for the reactivity of a stearic acid surface, a tube of 2·7 cm. diameter being used. The tube was coated with stearic acid under the conditions described above for paraffin wax and the initial pressure of each reactant was fixed at 200 mm. The

constancy of the velocity coefficients was good, there being no variation from the mean values greater than 5%. In two experiments the mean values were $4{\cdot}52 \times 10^{-4}$ and $4{\cdot}20 \times 10^{-4}$.

In Table V is a comparison of the relative surface reactivities measured by the ethylene–chlorine and by the ethylene–bromine reactions. These are referred to the reactivity of glass, taken as unity, by computing the ratios of the reactivities of the given surfaces to that of glass, the reactivity being measured, in the way described above, as the product of the bimolecular reaction coefficient and the diameter of the tube.

TABLE V.

Comparative surface reactivities by two methods.

Surface	Glass; gas dry.	Glass; gas wet.	Stearic acid; gas dry.	Paraffin wax with rubber.	Paraffin wax, optimum.
C_2H_4-Br_2	1·0	—	1·7	0·06	—
C_2H_4-Cl_2	1·0	1·3	1·06	0·076	0·0008

It will be seen that the results of the earlier work have been confirmed, while the prediction that the non-polar surface of paraffin wax is entirely unreactive has been practically demonstrated.

The results described above, when considered with reference to the adsorbed water layer which is known to exist at the surface of glass, would seem to have an important bearing on any explanation of the suspension of reactions by extreme drying. The adsorbed water layer, under " dry " conditions, is probably but one molecule thick, but tends to pile up as the vapour pressure is increased towards saturation point (McHaffie and Lenher, J., 1925, **127**, 1559). Hence, if we assume that the water layer is the polar catalyst in the case of the glass surfaces, we can explain the increased reactivity of moist gases as due to the more complete saturation of the surface water film. When the surface is covered with paraffin wax, it seems reasonable to assume that the water layer cannot form, in agreement with the fact that water shows no tendency to wet paraffin wax. There is thus no reaction, either with dry or with wet gases, a fact which shows also that no volume reaction sets in, in the presence of water vapour. It seems highly probable that we are here imitating the effects of Baker: by the extreme drying of his systems we may suppose that he was removing the water from the walls, while by using walls composed of a substance upon which water cannot condense we achieve the same result, even in the presence of moist gases. Finally, if a polar group such as carboxyl or hydroxyl be introduced into the paraffin molecule, we can imitate the effect of the water layer on glass; thus with walls composed of stearic acid, or cetyl alcohol, the surface becomes once more reactive.

If we inquire further as to the mechanism of the present reaction, there is little evidence to guide us. It seems probable, however, that the presence of water on the surface might cause a greater modification of the dielectric constant in the immediate vicinity of the surface than can be brought about by a single molecule in the ternary complex [A·H_2O·B], so that the whole reaction takes place through the medium of the adsorption layer, even in the presence of water vapour. It seems significant also that all the polar catalysts so far obtained contain oxygen, and we might regard their function as the formation of a complex with the chlorine molecule, through the medium of quadrivalent oxygen (*e.g.*, $\begin{matrix}H\\H\end{matrix}\!>\!O\!<\!\begin{matrix}Cl\\Cl\end{matrix}$) which, under the influence of the surface forces, is more dissociable than the chlorine molecule itself.

Summary.

A study has been made of the reaction between ethylene and chlorine, each at an initial partial pressure of 200 mm., at the surface of glass, paraffin wax, and stearic acid. By taking special precautions, a paraffin wax-surface was prepared showing a reactivity some 1200 times smaller than that of glass and about 70 times less than that previously found for a paraffin wax surface in the experiments on the union of ethylene and bromine. It has been shown that water vapour present at a partial pressure of 6 mm. increases the reactivity of the glass surface by 30%, whilst it has no effect on the paraffin wax surface. These results are discussed from the point of view of surface polarity and in the light of our knowledge of the adsorbed water film existing at the surface of many solid substances.

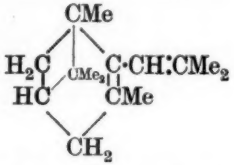
UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, November 26th,* 1925.]

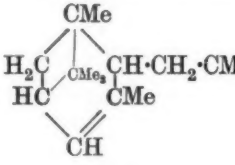
XIII.—*The Chemistry of the Caryophyllene Series. Part I.*

By GEORGE GERALD HENDERSON, JOHN MONTEATH ROBERTSON, and (in part) CARL ALOYSIUS KERR.

β-CARYOPHYLLENE belongs to the dicyclic series of sesquiterpenes, but as no naphthalene or benzenoid derivative can be obtained from it by the sulphur method (Ruzicka and Stoll, *Helv. Chim. Acta*, 1923, **6**, 854), it cannot be assigned to either of the known cadinene or eudesmol types. Its structure is therefore largely a matter of conjecture, although Semmler and Mayer (*Ber.*, 1911, **44**, 3657) consider that it consists of a mixture of two forms, for which, from

a study of the ozonide products, they have advanced formulæ I and II. The existence of the bridge ring system is, however, based upon the supposed identity of caryophyllenic acid with *cis*-2 : 2 : 3-trimethyl*cyclo*butane-1 : 3-dicarboxylic acid, and until this is definitely established these formulæ must be regarded as tentative.

(I.) 

 (II.)

Wallach and Walker (*Annalen*, 1892, **271**, 285) showed that caryophyllene forms a crystalline hydrate known as caryophyllene alcohol, $C_{15}H_{25}\cdot OH$, upon hydration with a mixture of sulphuric and acetic acids. The properties of this alcohol and in particular its relation to the hydrocarbon have not previously been fully examined. As there is some evidence that certain of its derivatives possess a different molecular configuration from that assigned to β-caryophyllene, experiments were carried out with a view to obtain more information in this connexion.

The alcohol prepared by the hydration method was found to be remarkably stable in certain respects. Thus, after heating with hydrogen peroxide for 52 hours, practically the whole of the alcohol was recovered unchanged. On treatment with permanganate the alcohol was again recovered unchanged. Towards bromine in chloroform solution it behaved as a fully saturated substance.

All dicyclic sesquiterpene alcohols of the formula $C_{15}H_{25}\cdot OH$ are unsaturated, uniting additively with bromine and being readily oxidised. It is evident that caryophyllene alcohol does not belong to this class, and therefore cannot be regarded as a direct hydrate of the hydrocarbon, as previously supposed. Apparently the hydrating agents have induced ring closure with the formation of a new tricyclic structure. Confirmation of this view is found in the fact that the alcohol can be formed through the agency of formic acid, which is a well-known means of effecting ring closure in the sesquiterpenes (Robertson, Kerr, and Henderson, J., 1925, **127**, 1944). Moreover, it has long been known that caryophyllene alcohol upon dehydration yields a hydrocarbon, clovene, which is not identical with caryophyllene, but which appears to be tricyclic from its physical properties (Wallach and Walker, *loc. cit.*).

Although it is not feasible to determine the molecular refractivity of caryophyllene alcohol directly owing to its high melting point (compare Semmler, *Ber.*, 1903, **36**, 1037), it appeared probable that the necessary information might be obtained from the physical

properties of certain of its esters, which were prepared in the course of this work. The following figures were therefore determined for the formate and the acetate, and they clearly indicate the tricyclic nature of the caryophyllene radical.

				$[R_L]_D$.			
Ester.	t.	$d_{4^\circ}^{t^\circ}$.	$n_D^{t^\circ}$.	Found.	Calc. for $C_{15}H_{25}$·R. Tricyclic.	Typical * $C_{15}H_{25}$·R. Dicyclic.	Calc. for $C_{15}H_{25}$·R. Dicyclic.
Formate, $C_{16}H_{26}O_2$†	7°	1·024	1·4998	71·78	71·02	—	72·75
Acetate, $C_{17}H_{28}O_2$‡	17°	1·003	1·4919	76·37	75 64	78·13	77·37

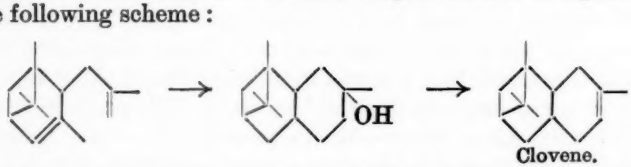
* Semmler and Jonas, *Ber.*, 1914, **47**, 2068, 2072.

† We wish to take this opportunity of correcting the density for the formate previously given (J., 1925, **127**, 1945), where $d_{4^\circ}^{17^\circ}$ 1·22 should be $d_{4^\circ}^{t^\circ}$ 1·024.

‡ Determined on the super-cooled liquid.

It will be observed that the exaltation found in the case of the caryophyllene derivatives is not greater than the corresponding divergence for a typical dicyclic member.

It is noteworthy that the limonene form (II) of active caryophyllene could readily adapt itself to such ring formation as is indicated by the above results. The course of the reaction and the dehydration of the alcohol to clovene may therefore be represented by the following scheme:



Clovene.

In addition to caryophyllene alcohol, Wallach's hydration method gives rise to a liquid product. We find this substance to consist of an unsaturated *hydrocarbon*, $C_{15}H_{24}$, b. p. 110—114°/9 mm., $d_{4^\circ}^{19^\circ}$ 0·9263, $n_D^{19^\circ}$ 1·5010, $[\alpha]_{5790\cdot3}^{16^\circ}$ −19·56°, which evidently differs from β-caryophyllene and is perhaps identical with the tricyclic caryophyllene obtained from the dihydrochloride by the quinoline method (Semmler and Mayer, *Ber.*, 1910, **43**, 3451) which had b. p. 122—123°/13 mm., $d_{4^\circ}^{20^\circ}$ 0·927, $n_D^{20^\circ}$ 1·50246, $\alpha_D^{20^\circ}$ −57°. Clovene, also regarded as tricyclic, has closely similar properties. The possible identity of these three substances is under examination.

Our experiments were next directed towards the synthesis of hydroxyl derivatives from caryophyllene corresponding to the dicyclic structure of the hydrocarbon, since it has been shown that Wallach and Walker's hydration method leads to ring closure. From caryophyllene dihydrochloride by the action of silver acetate in glacial acetic acid solution we obtained products which upon hydrolysis yielded an unsaturated *alcohol*, $C_{15}H_{25}$·OH, a saturated *glycol*, $C_{15}H_{26}(OH)_2$, and some regenerated hydrocarbon. The

alcohol, $C_{15}H_{25}\cdot OH$, which may be termed *caryophyllol*, has properties corresponding closely to those of a dicyclic sesquiterpene alcohol. Although it reacts with sodium, no ester has yet been obtained by any of the usual methods, which indicates that the alcohol is tertiary. By the action of a chloroform solution of bromine in the cold it is converted into a rather unstable *dibromide*, $C_{15}H_{26}OBr_2$.

The compound $C_{15}H_{26}(OH)_2$ is quite a stable substance, and is probably a glycol with both hydroxyl groups attached to tertiary carbon atoms. It possesses properties closely similar to those of cadinene glycol (Henderson and Robertson, J., 1924, **125**, 1992). The fact that the hydrocarbon product of the reaction gives a good yield of caryophyllene dihydrochloride on treatment with hydrogen chloride indicates that these hydroxyl derivatives also retain the dicyclic caryophyllene structure.

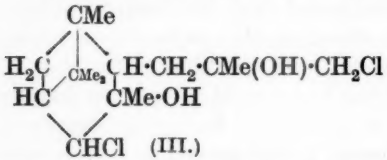
Wallach and Walker (*loc. cit.*) found that caryophyllene alcohol gives a series of halogen derivatives, of which the chloride, $C_{15}H_{25}Cl$, can be readily obtained. We have found that this compound also, as was to be expected from the above results, behaves as a fully saturated substance like the alcohol, and therefore must also be regarded as being tricyclic. It thus becomes of interest to enquire whether hydrogen chloride can be eliminated from this compound by any of the usual methods, because if this proved to be the case, a new type of tricyclic sesquiterpene would be expected, of which the above-mentioned compound would be the hydrochloride.

We have found that this chloride is much more stable than the known hydrochlorides of the sesquiterpene series. Even after prolonged heating in a concentrated alcoholic solution of sodium ethoxide, or with quinoline, practically all the compound was recovered unchanged. On treatment with sodium acetate in glacial acetic acid solution, however, chlorine was removed from the molecule, but the product of the reaction in this case proved to be the *acetate* of caryophyllene alcohol, $C_{15}H_{25}\cdot OAc$. Wallach and Tuttle (*Annalen*, 1894, **279**, 393) mention a caryophyllene acetate, but as no melting point or other data are given, it is impossible to state whether the compound we have obtained is similar to theirs.

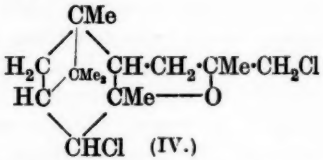
Since hypochlorous acid has proved of service in investigating the simpler terpenes (compare Slawinski, *Ber.*, 1899, **32**, 2064; Henderson and Marsh, J., 1921, **119**, 1492; Henderson and Kerr, J., 1924, **125**, 102), we examined the action of this reagent on β-caryophyllene. In this case, however, instead of using a dilute aqueous solution of the acid we adopted Detoeuf's method of preparing chlorohydrins (*Bull. Soc. chim.*, 1922, **31**, 102, 169, 176)

through the agency of chlorocarbamide, which in acid solution undergoes hydrolysis with formation of carbamide and hypochlorous acid. In order to regulate the reaction and to diminish the rate of hydrolysis of the chlorocarbamide, the caryophyllene was dissolved in 4—5 times its bulk of acetone. The first product of the reaction was not obtained in a pure state, but appeared to be a *dichlorohydrin* of caryophyllene, $C_{15}H_{24}Cl_2(OH)_2$. On treatment with acetic anhydride it yielded a small quantity of a *monoacetate*, but also in an impure state. When distilled at 1 mm. pressure, it was converted into a *saturated compound* of the formula $C_{15}H_{24}OCl_2$. This substance, a colourless liquid, appears to be the anhydride of the dichlorohydrin. The chlorine in this compound is not easily replaced, and oxidation with hydrogen peroxide yielded no definite product except some succinic acid.

If β-caryophyllene has the constitution (II) given above, the constitution of the dichlorohydrin may be represented by the formula (III) and that of the anhydride by (IV).



(III.)



(IV.)

It is true that the supposed anhydride does not undergo hydration to the corresponding glycol on treatment with dilute sulphuric acid, but Franke and Lieben (*Monatsh.*, 1914, **35**, 431) have shown that the anhydrides of 1 : 4- and 1 : 5-glycols are quite stable in this respect.

Experimental.

Preparation and Properties of Caryophyllene Alcohol.—The β-caryophyllene used in the following experiments was purified by fractional distillation (compare Robertson, Kerr, and Henderson, *loc. cit.*). To 1 litre of acetic acid containing 12 c.c. of sulphuric acid and 40 c.c. of water, 150 g. of caryophyllene were added and the whole was maintained at 80—100° for 30 hours. The product was steam distilled. At first acetic acid and an oil passed over, then the solid alcohol slowly distilled. After crystallisation from light petroleum at a low temperature it melted at 94—96° (yield, about 30%).

The liquid product of the hydration was collected by means of light petroleum and dried. On removing the solvent and allowing the product to remain 24 hours at 0°, a further quantity of the alcohol separated and was removed. The resulting oil was distilled under diminished pressure and the main fraction was finally redis-

tilled over sodium in a vacuum. The product consisted of a colourless oil with a pleasant odour which had b. p. 110—114°/9 mm., $n_D^{16°}$ 1·5010, $d_{4°}^{16°}$ 0·9263, $[\alpha]_{5790}^{16°}$ −19·56°. $[R_L]_D$ found, 64·8; calc. for a tricyclic sesquiterpene, 64·4 (Found: C, 87·7; H, 11·7. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%). This substance was unsaturated towards bromine.

Caryophyllene alcohol (50 g.) in glacial acetic acid (200 c.c.) and 30% hydrogen peroxide (55 c.c.) were heated together at 50—55° for 52 hours. The solution was then neutralised, when practically the whole of the caryophyllene alcohol was recovered unchanged. M. p. 94°. On standing in the cold with 1% permanganate the latter was not decolorised, and the alcohol was recovered unchanged. When the alcohol was gradually treated with bromine, both in chloroform solution at room temperature, no absorption or substitution could be detected.

Preparation and Properties of Other Hydroxyl Derivatives of Caryophyllene.—The dihydrochloride of caryophyllene was prepared by gradually treating caryophyllene (100 g.) in anhydrous ether (100 c.c.) with dry hydrogen chloride, the temperature of the reaction being kept at 0°. After remaining a further 24 hours at 0°, the ether was removed by passing a current of dry air over the surface of the liquid. On reducing the temperature to −20°, practically the whole of the liquid crystallised. Recrystallised from ethyl acetate, caryophyllene dihydrochloride had m. p. 69°, $[\alpha]_D^{16°}$ + 67° in 2·5% ethyl-alcoholic solution. Failure to observe the conditions stated, in particular with regard to temperature, results in a greatly diminished yield of the dihydrochloride.

A solution of caryophyllene dihydrochloride (50 g.) in glacial acetic acid (250 g.) was gradually treated with silver acetate (70 g.). The mixture was shaken for 2 to 3 hours at room temperature, and the reaction completed by gently warming on the water-bath. On cooling, the silver chloride was filtered off, and the acetic acid neutralised with sodium carbonate. The resulting product, consisting principally of acetates, was collected by means of ether and hydrolysed by warming with dilute methyl -alcoholic potash for ½ hour. After the alcohol had been distilled off, the product was rendered neutral with carbon dioxide and steam distilled. The portion volatile in steam was collected with ether, dried over anhydrous sodium sulphate, and distilled under reduced pressure. After several distillations, three principal fractions were obtained: (a) b. p. 122—130°/10 mm., (b) b. p. 130—140°/10 mm., and (c) b. p. 140—150°/10 mm. The fraction (a) consisted of regenerated caryophyllene. When treated with hydrogen chloride in the manner described above, an almost theoretical yield of the dihydrochloride,

m. p. 69°, was obtained. The fraction (c), which represented about 20% of the product, on further purification had b. p. 142—150°/10 mm., $d_4^{17°}$ 0·9632, $n_D^{17°}$ 1·5015; $[R_L]_D$ found, 68·03; calc. for a dicyclic sesquiterpene alcohol, 68·12 (Found: C, 80·6; H, 11·2. $C_{15}H_{26}O$ requires C, 81·1; H, 11·7%). This substance gave no solid derivative when treated in the usual manner with phthalic anhydride, or with phenylcarbimide, and therefore appears to be a tertiary alcohol. On boiling with acetic anhydride, dehydration occurred yielding a hydrocarbon. The alcohol is unsaturated towards bromine and alkaline permanganate. When slowly treated with bromine at 0°, both in chloroform solution, absorption occurred but no substitution was detected. The chloroform was removed under reduced pressure, leaving a colourless, oily dibromide (Found: Br, 40·1. $C_{15}H_{26}OBr_2$ requires Br, 41·8%) which slowly decomposed on exposure to light. The fraction (b) consisted of a mixture of the above alcohol and the hydrocarbon. A small higher-boiling fraction was also obtained, containing a higher percentage of oxygen, which probably consists of a mixture of the above alcohol with a small amount of the glycol referred to below.

The residue from the steam distillation contained a thick brown oil, which was repeatedly extracted with ether and dried. On removing the ether, most of this substance crystallised and by the addition of a small amount of light petroleum the remainder was deposited in minute, white needles. The substance was recrystallised from ether as a flocculent mass of minute needles, m. p. 173° (yield 3%). The composition corresponds with that of caryophyllene glycol, $C_{15}H_{26}(OH)_2$ (Found: C, 74·5; H, 11·7. $C_{15}H_{28}O_2$ requires C, 75·0; H, 11·7%). The substance is very soluble in alcohol, slightly soluble in ether, and almost insoluble in light petroleum. It does not decolorise bromine or alkaline permanganate solution.

Reactions of Chlorodihydrocaryophyllene.—The chloro-compound, $C_{15}H_{25}Cl$, was prepared by the action of phosphorus pentachloride on the alcohol (Wallach and Walker, *loc. cit.*) and purified by crystallisation from light petroleum. M. p. 63° (Found: Cl, 14·9. Calc., Cl, 14·8%). The yield was almost theoretical.

A portion was refluxed at 100° with a concentrated solution of sodium ethoxide for 12 hours. No action took place and the chloride was recovered unchanged. Another portion was heated at 210° in quinoline solution for 3 hours, but again the compound was recovered unchanged. A third portion (20 g.) was dissolved in glacial acetic acid (150 c.c.), and anhydrous sodium acetate (19 g.) gradually added. The solution was boiled for 3 hours. After 1 hour, sodium chloride began to be deposited. On cooling, the product was diluted with water and extracted with light

petroleum. After removing the solvent from the dried extracts, the product was distilled under reduced pressure, when a colourless oil was obtained, b. p. 149—152°/10 mm., which was saturated towards bromine. When mixed with light petroleum and cooled to −20°, a solid mass of small, white crystals separated, which on purification melted at 40°. The yield was nearly theoretical. This substance is fairly soluble in alcohol and in petroleum. Acid ethyl-alcoholic hydrolysis yielded ethyl acetate, and by hydrolysis with methyl-alcoholic potash a theoretical yield of caryophyllene alcohol, m. p. and mixed m. p. 95°, was obtained. The substance is therefore caryophyllene acetate, $C_{15}H_{25}O{\cdot}CO{\cdot}CH_3$ (Found: C, 76·8; H, 10·6. $C_{17}H_{28}O_2$ requires C, 77·2; H, 10·6%).

The Action of Hypochlorous Acid on β-Caryophyllene.—A solution of 108 g. of chlorocarbamide (2 mols.) in 300 c.c. of water was added slowly to a cooled solution of 120 c.c. of β-caryophyllene (1 mol.) and 10 c.c. of acetic acid in about 500 c.c. of acetone, and the mixture shaken for several hours until all the hypochlorous acid had disappeared. The acetone was then distilled off, the residual liquid extracted with ether, and the extract dried and distilled. The product, which presumably was the dichlorohydrin of β-caryophyllene, $C_{15}H_{24}(OH)_2Cl_2$, was a yellow, oily liquid, which could not be obtained in crystalline form, was not volatile in a current of steam, and could not be distilled without partial decomposition. The compound did not give a semicarbazone nor a nitrobenzoate, but when a portion was warmed with acetic anhydride (2 mols.) after addition of a drop of sulphuric acid reaction took place quickly. The product was extracted and after repeated distillation under diminished pressure yielded a colourless liquid, b. p. 190—200° of which the composition approximated to that of a monoacetate of the dichlorohydrin (Found: C, 57·1; H, 6·9; Cl, 19·9. $C_{17}H_{28}O_3Cl_2$ requires C, 58·1; H, 7·1; Cl, 20·2%). The supposed dichlorohydrin distilled at 1 mm. with little decomposition. Repeated fractionation finally yielded a colourless liquid, b. p. 125—140°/1 mm., which was essentially the anhydride of the dichlorohydrin (Found: C, 62·3; H, 7·9; Cl, 23·4. $C_{15}H_{24}OCl_2$ requires C, 61·8; H, 8·3; Cl, 24·3%).

This compound is saturated towards both bromine and potassium permanganate. It does not react with *p*-nitrobenzoyl chloride, with semicarbazide acetate, or with ammoniacal silver nitrate. It is not attacked by boiling aqueous 2% sulphuric acid or by dilute aqueous potassium hydroxide, but when heated with an aqueous alcoholic solution of the last reagent yielded an oily liquid which contained only a trace of chlorine, was unsaturated, and did not give the reactions of an alcohol.

Attempts to replace the chlorine in this compound by hydrogen were not successful. Addition of successive quantities of sodium amalgam to an alcoholic solution containing a trace of water resulted in the production of a yellow, oily liquid, which distilled for the greater part at 120—130°/1 mm., and still contained 14·20% of chlorine. Thus by this treatment approximately one atom of Cl was replaced ($C_{15}H_{25}OCl$ requires Cl, 13·8%). Prolonged heating of the compound with zinc dust and alcohol failed to yield a substance free from chlorine.

On oxidation with 30% hydrogen peroxide in glacial acetic acid solution the chloroanhydride yielded a small quantity of a viscous neutral product, some succinic acid, and another acid, in the form of a brown oily liquid, which has not been identified.

We are grateful to the Carnegie Trust for the award of grants which assisted us to prosecute this work.

UNIVERSITY OF GLASGOW. [*Received, November 14th*, 1925.]

XIV.—*The Density of Boric Oxide Glass and the Suspected Variation in the Atomic Weight of Boron.*

By HENRY VINCENT AIRD BRISCOE, PERCY LUCOCK ROBINSON, and GEORGE EDWARD STEPHENSON.

THROUGH the courtesy of Messrs. Borax Consolidated, Ltd., the authors, in 1922, were in possession of several parcels of boron minerals obtained from various parts of the world and containing a high percentage of boron. At that time an attempt was made to compare the atomic weights of the several specimens of boron contained in these minerals by preparing from each a specimen of boric acid, purifying these specimens by rigorous fractional crystallisation, and determining the density at 25·00° ± 0·02° of their aqueous solutions saturated at that temperature. The accuracy of the results as measured by their reproducibility fell short, however, of that necessary to give trustworthy evidence of any difference in atomic weight and this method of attack was abandoned.

Thereafter three of the samples of boron were used for determinations of the atomic weight by measurement of the ratio $BCl_3 : 3Ag$ which have already been reported (J., 1925, **127**, 700). These determinations gave evidence of an appreciable variation in atomic weight among the three samples. Therefore, as sufficient of all the original mineral samples was still available, a fresh attempt was made to obtain a comparative estimate of the atomic weights by deter-

mining the densities of samples of a solid boron compound prepared from the several sources. Of the available compounds, boric oxide glass appeared to be the most suitable; boric acid is easily prepared from the minerals, its low solubility in cold water renders its recrystallisation an excellent method of purification and it readily dehydrates to yield boric oxide glass, which, because of its chemical stability and transparent glassy character, seemed to be especially well suited to precise density determinations.

Although much attention has been given to the improvement of the specific gravity bottle (see, *e.g.*, Berkeley, J., 1907, **90**, 56; Baxter, *J. Amer. Chem. Soc.*, 1908, **30**, 46; Johnson and Adams, *ibid.*, 1912, **34**, 563), it is difficult to attain high accuracy in the determination of the density of solids by displacement methods. Moreover, as boric oxide is extremely hygroscopic, being in fact coated with an opalescent film of hydrated oxide in less than one minute when exposed to air of ordinary humidity, it is clear that the use of any form of specific gravity bottle for the determination of its density is attended by very serious difficulty. Therefore it was decided to use a modification of the flotation method suggested by Andreae (*Z. physikal. Chem.*, 1911, **76**, 491). Beads of pure boric oxide glass prepared from each of six sources, with all precautions to exclude traces of moisture, were sealed up in tubes containing the same mixture of dry, inert organic liquids of suitable density; then careful observations were made of the *temperature* of flotation of the beads of each sample. Separate determinations of the density and thermal expansion of the liquid mixture enabled the actual densities of the boric oxide samples to be calculated. Thence, using the ascertained atomic weight of the boron in one sample as a standard, it was possible, assuming identity of atomic volume for all specimens of boron, to calculate the atomic weights of the specimens of boron in the remaining samples.

Experimental.

Preparation of Beads of Pure Anhydrous Boric Oxide.—The sources of the various samples were:

No. 1. Calcined borate of lime; Ascotan, Chile.
No. 2. Calcined colemanite; Death Valley, California, U.S.A.
No. 3. Borate of lime; the Argentine.
No. 4. Borate of lime; Peru.
No. 5. Boracite; Sultan Tchair, Asia Minor.
No. 6. Crude boric acid; Volterra, Italy.

Samples 1 to 5 were separately treated as follows: 200 g. of mineral were dissolved as far as possible in hot 10% hydrochloric

acid, the solution was filtered hot, cooled quickly, and the precipitated boric acid was removed by filtration. The acid was twice recrystallised from pure water, the product was fused in platinum and then dissolved in pure hot water and allowed to crystallise. From this stage all the samples of boric acid, including No. 6, were twice recrystallised from pure water and each batch of crystals was tested for purity.

Owing, presumably, to the insolubility of calcium borate and the comparative insensitivity of available tests for calcium, no trace of that metal could be detected in the boric acid even at an early stage of the purification, but sulphate and chloride were then present in detectable amounts. Therefore the progress of purification in the later crystallisations was followed by tests for sulphate and chloride, and the apparent absence of these radicals in the final main crops of boric acid and in the mother-liquors whence these had come was taken as an indication of high general purity. The purified boric acid was stored in clean stoppered bottles, capped to exclude dust.

In the preparation of beads 10 g. of each sample were fused for 4—5 hours in a *suitable* covered platinum crucible heated at about 900° in an electric muffle furnace. The term *suitable* is stressed because it was only after several trials that a platinum crucible was found from which iron was not leached by the melt. Even after this drastic treatment, boric oxide still contains water, presumably because the high viscosity of the melt hinders its escape, and in order to dehydrate the material completely and prepare suitable individual samples for flotation, the crucible was again heated over a Méker burner and a quantity of the fused oxide was collected on a platinum wire. This was heated in a hot bunsen flame for 1 minute and if it then showed no sign of bubbles—a clear indication of the complete absence of water—it was allowed to drop from the wire directly into a clean cold platinum basin, which had been previously heated to redness and then rested in a desiccator over phosphoric oxide, the lid of the desiccator being raised for the minimum time. When bubbles appeared in a bead, the material was rejected, as it was found that such beads could be almost completely volatilised before losing their vesicular structure. The beads were about 3 mm. in diameter and from 30—35 were prepared from each sample. A number of test beads examined under the microscope were isotropic, contained no visible bubbles and, between crossed Nicols, appeared free from strain.

Preparation of the Flotation Liquid.—No single liquid of suitable chemical nature having the required density could be found, so a binary mixture was used. It appeared that the constituents of this mixture should be chemically stable and non-reactive, should be

capable of being thoroughly dried by means of phosphoric oxide, should have densities slightly below and above 1·8, should have closely similar and preferably rather high boiling points and fairly low viscosities. The requirements of the case were met by a mixture of pentachloroethane (b. p. 161·7°, D 1·693) and trimethylene dibromide (b. p. 165·0°, D 1·987) containing 61·07% by volume of the former liquid. Both liquids were obtained from Messrs. British Drug Houses, Ltd.; and were further purified by fractional distillation, about 20% being rejected as head and tail fractions. The main fraction of pentachloroethane was collected between 160° and 162·5° at 762·6 mm. and that of trimethylene dibromide between 164·0° and 167·0° at 762·6 mm.

FIG. 1.

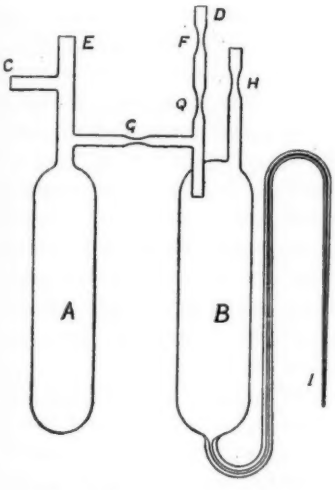
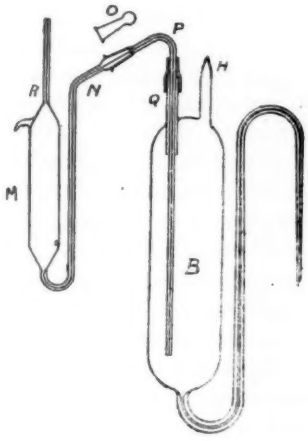


FIG. 2.

FIG. 3.



About 120 c.c. of the mixture were left in contact with phosphoric oxide for 24 hours. Slight decomposition and darkening occurred, probably owing to slight conversion of trimethylene dibromide into propylene dibromide (b. p. 141·7°, D 1·9), but the method of experiment ensured that any change in the density or volatility of the mixture thus produced would have no effect on the density found for boric oxide.

The apparatus used for the final purification and preservation of the flotation mixture is shown in Fig. 1. Both it and the other apparatus to be described later were constructed throughout of "Durosil" glass and before use were soaked in a solution of chromic acid in strong nitric acid, washed very thoroughly with pure water, dried in an air-oven at 150°, and finally swept out for some time

with a slow stream of air which had been cleaned by bubbling through concentrated aqueous potash and dried by passage over solid caustic potash and phosphoric oxide. The tubes at H and I being temporarily sealed by fusion, a stream of dry air was passed in at C and out through a phosphoric oxide guard-tube on D, and the liquid mixture was introduced through E into the vessel A : tubes E and C were then sealed. A was cooled with ice and the apparatus was evacuated by a Gaede pump through D, which was finally sealed off at the constriction F. At this stage the liquid was almost completely distilled from A to B. Then both A and B were cooled with ice, dry air was slowly admitted at C, and the vessel B was sealed off from A at G. The reason for thus admitting air was to displace the vapour of the organic liquids from the connecting tube before sealing off : in this way perfectly clean seals were obtained, whereas the vapour, if present, carbonises when heated to redness. The vessel B was stored in a dark place until required.

Filling of the Flotation Tubes.—These tubes, of the form shown in Fig 2, were constructed of very thin-walled Durosil tubing of about 8 mm. bore, had a fine bent capillary at J, and were slightly constricted at L and K. The length of the tube between K and J was about 30 cm. Each tube bore an etched number corresponding with the sample of boric oxide it was to contain, and was charged with beads as follows : While dry air was passed through J up the perfectly clean and dry tube, beads, from 30—35 in number, of one sample of boric oxide were quickly removed from the phosphoric oxide desiccator and poured into this tube : the tube was then immediately sealed off first at L and then at J.

The procedure for filling the tubes with liquid was necessarily elaborate, but worked without a hitch in practice. A large aspirator bottle, containing a quantity of loose phosphoric oxide and air under slight pressure, was connected to the sealed tip of F (previously scratched with a file) by pressure tubing, through a train consisting of a tap, a phosphoric oxide guard-tube and a T-piece opening to the atmosphere by means of a tap and phosphoric oxide guard-tube on the side limb. The apparatus having been very thoroughly dried, pressure was raised in the aspirator and the whole was allowed to stand for over an hour to ensure adequate drying of the additional air. Thereafter the tip F was broken inside the rubber tube and the fine delivery tube I was also opened near the tip and at once inserted in a guard-tube carrying a current of dry air. Then each flotation tube in turn was cracked just below L by means of a sharp file and a hot rod, the top was lifted off, a fine bent tube delivering a current of dry air was passed down below the constriction K, and then the flotation tube was slipped quickly over

the jet I of the reservoir B, from which the guard-tube had been that instant removed. By admitting air from the aspirator, liquid was forced over from B until the flotation tube was filled to a depth of about 20 cm. The flow of liquid was stopped by shutting off B from the aspirator and releasing the pressure in B by opening to the air the guarded tap in the connecting train. Then the flotation tube was withdrawn from I (and replaced immediately by the guard-tube), the fine tube delivering air was lifted just above the constriction K, and the flotation tube was sealed with the blow-pipe at that point.

After the drill had been mastered by practice runs on blank apparatus, this procedure occupied much less time than it takes to describe. In the final experiments, the time required to fill a tube averaged four minutes, and no one tube was open for more than 4½ minutes.

Determination of the Density and Thermal Expansion of the Liquid.—For this purpose a special pyknometer of the form shown at M (Fig. 3) and holding about 10 c.c. was used. It had at N a taper ground carefully to fit both the cap, O, and the bent extension tube, P, and at R a fine engraved reference mark. Both tubes of the pyknometer were of very fine bore. It was weighed against a precisely similar pyknometer as tare, on a balance having a sensitivity of 20 scale divisions per mg., by means of a set of weights carefully calibrated in air for atomic weight work.

Five determinations of the weight of the pyknometer empty, made after various washings, fillings and immersions in the thermostat bath, gave concordant results, and thus afforded evidence that the error of weighing was probably insignificant. The weights of the pyknometer filled with pure water at 17·00° and 19·45° were determined in triplicate and thus, by means of the known specific volume of water, the absolute volume of the pyknometer at these temperatures was ascertained.

In filling the pyknometer with the flotation liquid the reservoir B (Fig. 3) was opened at Q, the carefully dried extension tube P (closed at the ground end by means of a rubber cap) was slipped in, and an air-tight joint made by sliding the wired-on rubber sleeve over the tube P. The reservoir was opened through a phosphoric oxide guard-tube at H. Both reservoir and pyknometer were then clamped to a retort stand and immersed over the barrels in the water of the thermostat tank maintained at $17{\cdot}00° \pm 0{\cdot}02°$. After 20 minutes, the retort stand was lifted from the bath, the pyknometer was connected by the ground joint N to the reservoir and filled with liquid forced over by admitting dry air through H. Then the pyknometer was disconnected and P was closed with its rubber cap.

These operations having been carried out very quickly, the stand and vessels were returned to the thermostat and held at 17·00° for a further 30 minutes. Then the liquid level in the pyknometer was adjusted by drawing off the excess with a piece of pure filter-paper, and the pyknometer was stoppered, removed from the bath, dried carefully, and weighed with all due precautions. It was then replaced in the thermostat, maintained at 19·45° ± 0·02° for 40 minutes, the liquid level was again adjusted, and the pyknometer was stoppered, dried, and weighed as before.

These determinations gave the data necessary to ascertain with the requisite precision the absolute density of the liquid at two temperatures, comprising between them the range of flotation temperatures. The density at intermediate temperatures was obtained on the assumption, clearly justifiable for so short a temperature range, that the relation of density to temperature is linear, and was read from a large-scale graph.

Determination of Temperature of Flotation.—The six flotation tubes, together with an open-scale thermometer graduated in 0·1°, were mounted vertically by means of rubber bands on two horizontal rods clamped to a retort stand. The whole apparatus was then immersed in a copper tank, with plate glass sides, containing about 27 litres of water. The tank was fitted with a motor-driven paddle, and at about room temperature this arrangement proved to be sufficiently thermostatic for its purpose. In a preliminary test, the temperature was raised slowly from about 17° to about 19·5° by the addition of quantities of 100 c.c. of hot water at regular intervals, and the approximate temperatures of flotation of the several samples of beads were observed. The final observations were made in each tube separately, and the temperature at which the beads remained suspended was noted for each sample. In all cases one or two beads—never more—whilst of the same order of density, appeared to be slightly heavier than the rest and sank first. The movement of the next lot in order of density, usually upwards of 6 (which were followed down almost immediately by the main bulk), was therefore observed with the aid of a fixed telescope, and the bath temperature was carefully regulated until they were brought to rest midway in their fall through the liquid. These beads were maintained stationary in suspension for 30 minutes and the temperature was observed every 3 minutes : these temperature readings did not vary over a greater range than 0·02° and the mean value was taken as the flotation temperature.

As the beads floated for ½ hour at a substantially constant temperature, it is evident that they must have been in thermal equilibrium with the liquid. Any small defect in this respect would have

a negligible effect on the results owing to the smallness of the thermal expansion of boric oxide glass. Samsoen (*Compt. rend.*, 1925, **181**, 354) has shown that up to 240° this has a value about 15×10^{-6}, whence a change of temperature of 0·1° (which is large in relation to the present measurements) changes the density of the glass by about one unit in the eighth decimal place.

Further, the prompt movement of the beads when the slightest perceptible change was made in the bath temperature showed that the flotation liquid within the tubes acquired the temperature of the bath with very little delay, probably within one minute. This is the more probable because other experiments in progress in these laboratories have shown that some 60—100 c.c. of liquid contained in a sealed tube 30 mm. in diameter with walls 1½ mm. thick, without agitation, requires only some 8—15 minutes to acquire within 0·01° the temperature of a water-bath in which it is wholly immersed.

Results.

The following values for the density of the liquid, relative to water at 4°, are each the mean of two concordant determinations :—

Temperature	17·00°	19·45°
Volume of pyknometer	9·7822 c.c.	9·7825 c.c.
Weight of liquid contained by pyknometer	17·5858 g.	17·5471 g.
Density of liquid	1·79773	1·79372

The table given below shows for each sample of boric oxide the flotation temperature, the corresponding density, the atomic weight calculated from the density, and, in the case of three samples, the atomic weight derived from determinations of the ratio $BCl_3 : 3Ag$ using boron trichloride prepared from the same original sample. In calculating the atomic weight corresponding to the ascertained density, sample 5, derived from boracite from Sultan Tchair, Asia Minor, was taken as standard, with the atomic weight B = 10·818. Hence for any other sample, X, the atomic weight is found by :

$$\text{At. wt. of boron in X} = \tfrac{1}{2}\left(\frac{\text{Density of X} \times \text{Mol. wt. of standard } B_2O_3}{\text{Density of standard } B_2O_3} - 48\right).$$

Sample No.	Place of origin.	Flotation temp.	Density.	Relative atomic weight. Calc. from density.	Relative atomic weight. Determined from ratio $BCl_3 : 3Ag$.
2	California	17·36°	1·79711	10·847	10·841
6	Tuscany	18·15	1·79583	10·823	10·825
5	Asia Minor	18·30	1·79558	10·818 (standard)	10·818
1	Chile	18·30	1·79558	10·818	
3	Argentine	18·65	1·79501	10·806	
4	Peru	19·25	1·79404	10·788*	

* The beads of this sample showed a considerably greater variation in density among themselves than was observed in the case of the other samples. Hence the authors attach less weight to this figure than to the data for samples 1—5 inclusive.

Discussion of Results.

The method of determining densities here described may clearly be made to yield extremely precise results and is applicable to a great variety of solids, provided that a suitable flotation liquid can be obtained. The values recorded show that the mean density of pure fused boric oxide is 1·7952 and that the value 1·88 commonly used is considerably in error.

The estimated maximum error in the determination of the specific gravity of the flotation liquid is $\pm$ 0·00008: the actual error is probably rather less at temperatures intermediate between 17·00° and 19·45°. Owing to the means adopted to ensure that all the flotation tubes were filled at one time from the same well-mixed bulk of liquid, the *relative* values of the specific gravity deduced from the flotation temperatures are probably uncertain only in so far as those temperatures are uncertain. It is unjustifiable to attempt to report in detail the very numerous and detailed records of the observations of flotation temperatures, but they have been subjected to the most critical examination by the three authors working independently and the utmost difference of opinion thus elicited in their interpretation would not affect by one unit the third decimal of the atomic weight in any case. Hence it seems probable that the relative densities have an error less than 1 part in 10,000 parts, and that the maximum error in the relative values of the atomic weight does not exceed four or five units in the third decimal.

Admitting the view here expressed as to the precision of these results, the observed differences among them require explanation. The authors believe that the samples of boric oxide are very pure and, moreover, that the uniformity so carefully observed in their purification and subsequent treatment should have ensured that any impurity, for example, a possible trace of water, which they may have retained can have had little influence on the *relative* values found for their densities. Hence the observed differences are attributed to a variation in the atomic weight of one of the elements present and as there exists no evidence that such variation is possible in the case of oxygen, it is assumed to occur in the atomic weight of boron. The good agreement in three cases between the relative atomic weights deduced from the density values and found by the determination of the ratio $BCl_3 : 3Ag$ (Briscoe and Robinson, J., 1925, **127**, 696) can scarcely be accidental, and the authors believe that the present work confirms the conclusions drawn in the paper cited.

If these atomic weight values are correct, it is remarkable that the atomic weights of boron from the Argentine and Peru are very appreciably lower than any values hitherto recorded.

Evidently a determination of the boron halide : silver ratio for material from these sources would constitute a valuable check on the present results and conclusions, and the authors have considered undertaking this investigation. It appears to them, however, that any further work they might do on the atomic weight of boron can add but little to the value of the evidence they have already advanced, and that they should now leave it to other chemists to confirm or refute the conclusion, drawn from that evidence, that boron, like lead, has an atomic weight varying with its source. It is much to be hoped that this further investigation will be undertaken.

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XV.—*Butyl Esters of the Simpler Amino-acids. Part I.*

By WALTER THOMAS JAMES MORGAN.

HITHERTO, with few exceptions, only the ethyl esters of the amino-acids have been prepared and examined (Curtius, *Ber.*, 1883, **16**, 753; 1884, **17**, 953; *J. pr. Chem.*, 1888, **37**, 150; Fischer, *Ber.*, 1901, **34**, 433). Butyl esters have now been prepared. These are more stable than the corresponding ethyl esters—inasmuch as quantities up to 20 g. distil almost completely, whereas ethyl esters distilled under similar conditions invariably leave a brown residue —and are much less volatile in ether vapour under diminished pressure. They should be, therefore, the more suitable form in which the monoamino-acids produced by the hydrolysis of proteins may be estimated. Since the application of this method for the separation of the monoamino-acids of protein is now unavoidably postponed, it seems desirable to publish the work so far completed.

EXPERIMENTAL.

n-*Butyl Glycine Hydrochloride.*—Glycine (5 g.) suspended in 100 g. of dried and carefully fractionated butyl alcohol was esterified by the method of Curtius (*Ber., loc. cit.*). Several similar preparations of the hydrochloride were made using the dry lead salt of the acid. The finely divided lead chloride that separates has, according to Foreman (*Biochem. J.*, 1919, **13**, 378), a favourable catalytic effect

on the rate of esterification. The mixture saturated with hydrogen chloride was heated on a boiling water-bath until the amino-acid dissolved, the excess of butyl alcohol was then distilled under reduced pressure, and the pale yellow syrup of the *ester hydrochloride* crystallised from ethyl acetate. The solid so obtained was quickly ground, kept for 2 days over solid potassium hydroxide, and crystallised from ether–ethyl acetate (1 : 2), separating in flat laminæ, m. p. 69—71°. (All melting-point determinations were carried out in sealed capillary tubes owing to the hygroscopic nature of the ester hydrochloride.) It dissolved readily in water, alcohol, acetone, or ethyl acetate, but was only sparingly soluble in ether or chloroform (Found : N, 8·2; Cl, 21·1. $C_6H_{14}O_2NCl$ requires N, 8·3; Cl, 21·2%).

n-*Butyl Glycine*, $NH_2{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}C_4H_9$.—To a vigorously shaken suspension of the hydrochloride (21·5 g.) in dry ether (250 c.c.) at 0°, anhydrous baryta was added, in portions of about 1 g., until it was in excess; even so, some hydrochloride remained, but this decomposed on addition of 5 c.c. of 70% potassium hydroxide solution. The whole was immediately shaken and filtered and the residue, consisting of baryta, barium chloride and a little undissolved ester, was shaken with two further quantities of ether. The combined ethereal filtrates were concentrated under reduced pressure to about 40 c.c., the temperature being kept below 30° to prevent volatilisation of the ester with the ether vapour. The ester distilled at 81—81·5°/18 mm. as a colourless oil having the characteristic odour of all amino-acid esters (yield, 14 g. or 83%; $d^{16°}$ 0·9703). The ester is soluble in water, ether, or alcohol (Found : N, 10·6. $C_6H_{13}O_2N$ requires N, 10·7%).

In a sealed glass tube, the freshly distilled ester (5 g.) changed completely in 24 hours into a white, crystalline solid. This substance gave an intense biuret reaction, charred without melting at 240°, and was insoluble in alcohol, chloroform, glacial acetic acid, or benzene but fairly easily soluble in hot water (Found in material washed free from butyl alcohol : C, 48·6; H, 7·7. Triglycylglycine butyl ester requires C, 47·7; H, 7·3%). A further preparation of this compound is being carried out, when it is hoped to recrystallise the substance and determine its molecular weight.

The *picrate* was prepared by warming together at 60° for ¼ hour an alcoholic solution of the ester (3 g.) and a solution of picric acid (5·2 g.) in 50% alcohol. On cooling, the *picrate* separated in pale yellow laminæ, m. p. 113°, which were very soluble in acetone, somewhat soluble in chloroform or ether, and insoluble in light petroleum or ligroin (Found : N, 15·6. $C_{12}H_{16}O_9N_4$ requires N, 15·5%).

The *benzoquinone* derivative, $(C_4H_9{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}NH)_2C_6H_2O_2$,

separated in scarlet needles from the dark red solution produced by the interaction of the ester (3 g.) and benzoquinone (4 g.) in ether at 0°. The crystals were washed with ether and freed from quinol by dissolution in chloroform; the quinone compound, m. p. 179—180°, was precipitated from the solution by light petroleum (Found: N, 7·6. $C_{18}H_{26}O_6N_2$ requires N, 7·6%).

n-*Butyl carbamidoacetate*, $H_2N{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}C_4H_9$, separated in tufts of colourless needles, m. p. 119°, when butyl glycine hydrochloride (2·8 g.), dissolved in a minimum of water, was warmed with a solution of potassium cyanate (1·7 g.) on a water-bath. It was soluble in hot ethyl alcohol, sparingly soluble in cold acetone, and insoluble in light petroleum or ligroin (Found: N, 16·1. $C_7H_{14}O_3N_2$ requires N, 16·2%).

iso*Butyl Glycine Hydrochloride*.—A suspension of glycine (15 g.) in dry *iso*butyl alcohol (250 c.c.) was saturated with hydrogen chloride, and solution completed by heating on a boiling water-bath for ½ hour. The subsequent procedure was as described in the case of the *n*-butyl ester hydrochloride. The *hydrochloride*, m. p. 84—88°, is very hygroscopic and quickly liquefies on exposure to air. It is readily soluble in alcohol or ethyl acetate, but only sparingly soluble in ether or chloroform (Found: N, 8·4; Cl, 21·2. $C_6H_{14}O_2NCl$ requires N, 8·4; Cl, 21·2%).

iso*Butyl glycine* was obtained from its hydrochloride (37 g., recrystallised from ether–ethyl acetate [2 : 1] and dissolved in 750 c.c. of dry ether) in the same way as the normal ester. The ether was dried over anhydrous potassium sulphate. The pure *ester* is a colourless, oily liquid with a characteristic odour (yield, 73%), b. p. 79·5—80·5°/18 mm., $d^{20°}$ 0·9609, $d^{17°}$ 0·9618. It is readily soluble in water, alcohol, or chloroform (Found: C, 54·9; H, 9·9. $C_6H_{13}O_2N$ requires C, 55·1; H, 9·9%).

The *picrate* was obtained by warming together an alcoholic solution of the ester (2 g.) and an aqueous-alcoholic solution of picric acid (1 mol.) and pouring the mixture into water. The *picrate* was crystallised from benzene, dried in a vacuum desiccator, and, as the melting point was not sharp, recrystallised from alcohol and was thus obtained in needles, m. p. 82—87°. It was only slightly soluble in ether or light petroleum (b. p. 40—60°) and insoluble in ligroin (Found: N, 15·5. $C_{12}H_{16}O_9N_4$ requires N, 15·5%).

The *benzoquinone* derivative was prepared and purified as was the preceding isomeride. The scarlet needles obtained, m. p. 171—172°, were insoluble in hot or cold water or ligroin, somewhat soluble in ether, and readily soluble in cold chloroform or 50% aqueous alcohol (Found: C, 59·2; H, 7·3; N, 7·7. $C_{18}H_{26}O_6N_2$ requires C, 59·0; H, 7·1; N, 7·7%).

Unless stated otherwise, the following substances were prepared in essentially the same ways as the corresponding compounds already described.

n-*Butyl* dl-*Alanine Hydrochloride.*—Prepared from racemic alanine (15 g.) and recrystallised from ethyl acetate, this compound melted at 58—61° (sealed tube), rapidly deliquesced in moist air, and was only slightly soluble in ligroin or ether but readily soluble in ethyl alcohol, benzene, chloroform, or acetone (Found : N, 7·7; Cl, 19·5. $C_7H_{16}O_2NCl$ requires N, 7·7; Cl, 19·6%).

n-*Butyl* dl-*alanine* was obtained as a colourless, oily liquid, b. p. 81·5—82°/16 mm., $d^{19°}$ 0·9342 (yield 66%), having the usual characteristic odour. It is soluble in water, ether, alcohol, or chloroform. After being kept in a sealed glass tube for 3 weeks, the ester showed no signs of anhydride formation (Found : N, 9·7. $C_7H_{15}O_2N$ requires N, 9·6%).

The *picrate*, m. p. 124°, crystallised in needles from 30% and 50% alcohol and in opaque, dendritic crystals from 5% alcohol (Found : N, 14·7. $C_{13}H_{18}O_9N_4$ requires N, 14·9%).

Several attempts were made to isolate the benzoquinone derivative. A solution of the ester and benzoquinone in dry ether developed a bright scarlet colour, but after cooling for several hours in a freezing mixture nothing separated; on cooling in solid carbon dioxide and ether, crystals of quinol were deposited. Evaporation of the ether solution gave only a red syrup which could not be crystallised. Precipitation with light petroleum gave only a dark red oil. The isolation of this compound is being further studied.

iso*Butyl* dl-*Alanine Hydrochloride.*—The syrup obtained was very difficult to crystallise even after drying in a vacuum desiccator over phosphoric oxide. Precipitation with ether of a solution of the hydrochloride in ethyl acetate gave a syrupy liquid which crystallised in flat, soft, soapy plates, m. p. 60—63° (sealed tube), which changed into a syrup on being exposed to air for a few minutes (Found : N, 7·6. $C_7H_{16}O_2NCl$ requires N, 7·7%).

iso*Butyl* dl-*alanine*, prepared from the ester hydrochloride (31 g.) and distilled at 77—78°/19 mm., was a colourless, oily liquid soluble in water, alcohol, ligroin, or chloroform (yield 95%); $d^{18°}$ 0·9330 (Found : N, 9·7. $C_7H_{15}O_2N$ requires N, 9·6%).

As in the case of the *n*-butyl ester, all attempts to isolate the quinone derivative failed.

The *picrate* was obtained quantitatively in small, flat plates, m. p. 132—133°, by warming the ester (2·5 g.) with a solution of picric acid (3·6 g.) in 50 c.c. of 50% alcohol at 70—80° for ½ hour and cooling over-night. It was soluble in alcohol, ether, or acetone,

sparingly soluble in chloroform, and insoluble in light petroleum or ligroin (Found : N, 15·1. $C_{13}H_{18}O_9N_4$ requires N, 15·0%).

n-*Butyl* dl-*Valine Hydrochloride*.—Prepared from *dl*-valine (5 g.) and crystallised from ethyl acetate, the *hydrochloride* was obtained in colourless, deliquescent needles, m.p. 59—60°, which were readily soluble in alcohol or acetone and sparingly soluble in dry ether or light petroleum (Found : N, 6·7. $C_9H_{20}O_2NCl$ requires N, 6·7%).

n-*Butyl* dl-*valine* was obtained from the hydrochloride (3·5 g.) in the usual way; the combined ethereal filtrates were dried with anhydrous sodium sulphate and the ether was evaporated below 25°. The *ester*, b. p. 98—98·5°/17 mm., $d^{14°}$ 0·9266, was a colourless, syrupy liquid (yield 97·5%) having the usual characteristic odour. It was soluble in water, alcohol, ether, or chloroform (Found : N, 8·3. $C_9H_{19}O_2N$ requires N, 8·1%).

The *picrate* formed long, yellow needles, m. p. 91—92°, which were soluble in acetone, ether, or chloroform, somewhat soluble in benzene, and insoluble in light petroleum (Found : N, 13·9. $C_{15}H_{22}O_9N_4$ requires N, 13·9%).

n-*Butyl* dl-*Leucine Hydrochloride*.—Leucine (6 g.) was esterified in the usual manner. After standing in the ice-chest for 48 hours, the alcoholic solution deposited flat, colourless plates, which were recrystallised from ether and dried in a vacuum desiccator; m. p. 110—111°. The *hydrochloride* was exceedingly hygroscopic, and very soluble in alcohol but only slightly soluble in chloroform or ether. It crystallised from ethyl acetate in stellate clusters of colourless needles (Found : N, 6·4; Cl, 16·0. $C_{10}H_{22}O_2NCl$ requires N, 6·3; Cl, 15·9%).

n-*Butyl* dl-*leucine*, prepared from the hydrochloride (4 g.), was a clear, colourless, oily liquid (yield 69%), b. p. 113·5°/18 mm., $d^{15·5°}$ 0·8733, which was soluble in water, alcohol, ether, or chloroform (Found : N, 7·4. $C_{10}H_{21}O_2N$ requires N, 7·5%).

The *picrate* was obtained in yellow needles, m. p. 139°, which were soluble in alcohol, ether, or acetone and insoluble in ligroin or benzene (Found : C, 46·1; H, 13·6. $C_{16}H_{24}O_9N_4$ requires C, 46·2; H, 5·8; N, 13·5%).

iso*Butyl* dl-*Leucine Hydrochloride*.—This compound was a clear, colourless syrup which slowly crystallised on standing for 2 or 3 days over solid caustic potash in a vacuum desiccator; it was recrystallised from ethyl acetate, washed with ether, and again dried in a vacuum desiccator (yield 81%); m. p. 97—99° (Found : N, 6·3; Cl, 15·7. $C_{10}H_{22}O_2NCl$ requires N, 6·3; Cl, 15·9%).

iso*Butyl* dl-*leucine*, b. p. 110°/19 mm., $d^{18·4°}$ 0·9066, was obtained as a colourless, oily liquid (yield 88%) which was soluble in alcohol,

chloroform, or ether (Found : C, 64·1; H, 11·0; N, 7·4. $C_{10}H_{21}O_2N$ requires C, 64·2; H, 11·2; N, 7·5%).

The *picrate* crystallised from dilute alcohol in flat plates, m. p. 135—136°, which were soluble in hot water, chloroform, or ethyl alcohol, slightly soluble in cold water or ether, and insoluble in light petroleum (Found : C, 46·0; H, 6·0; N, 13·6. $C_{16}H_{24}O_9N_4$ requires C, 46·2; H, 5·8; N, 13·5%).

The author wishes to express his gratitude to Dr. G. Dean for his kind interest at all times, and to the Chemical Society for assistance in the purchase of materials.

WEST HAM MUNICIPAL COLLEGE. [*Received, August 6th*, 1925.]

XVI.—*The Nitration of β-Naphthoic Acid and Some New Amino- and Nitro-naphthoic Acids.*

By HAROLD AINSWORTH HARRISON and FRANK ALBERT ROYLE.

The Nitration of β-Naphthoic Acid.

THE earliest work on the nitration of β-naphthoic acid was carried out by Kuchenmeister (*Ber.*, 1870, **3**, 740), and by Ekstrand (*ibid.*, 1879, **12**, 1393), but yielded little if anything of permanent value. Later, Ekstrand (*J. pr. Chem.*, 1890, **42**, 273), by fractional crystallisation of the mixture of ethyl esters obtained from the crude nitration product, isolated five supposedly distinct compounds. Of these, one (m. p. 111°) gave a free acid, m. p. 295°, which was identical with that previously prepared by Graeff (*Ber.*, 1883, **16**, 2252) from the nitration product of β-naphthonitrile, and was shown to be 8-nitro-2-naphthoic acid. The second ester (m. p. 121°; free acid, m. p. 288°) was that of 5-nitro-2-naphthoic acid. From the small fractions which remained, one ester melting at 75° was isolated (free acid, m. p. about 285°), and two others were described in the following year (*ibid.*, 1891, **43**, 409); of these, one melted at 92° (free acid, m. p. 272° [279°] *) and the other at

* This nitro-acid on reduction gave an aminonaphthoic acid, m. p. 211°. Now 5-amino-1-naphthoic acid melts at this temperature, and the 5-nitro-isomeride is to be expected from the nitration of α-naphthoic acid, if any occurred as impurity in Ekstrand's initial material. Further, 8-nitro-1-naphthoic acid, which would also be formed, cannot be esterified by the method employed (hydrogen chloride in alcoholic solution; compare Ekstrand, *ibid.*, 1888, **38**, 156) and therefore would not appear in the esterified mixture. Finally, the ethyl ester of 5-amino-1-naphthoic acid melts at 92° (compare above). The free nitro-acid, however, melts at 242° (Graeff, *loc. cit.*, p. 2250).

131°. (This last ester charred when warmed with sulphuric acid in the usual way, and the corresponding nitro-acid was not isolated.) No constitutions were assigned by Ekstrand to these isomerides.

Of the seven possible mononitro-derivatives of β-naphthoic acid, Ekstrand had thus claimed to have detected the presence of five. These did not include the 1-nitro-compound, m. p. 239°, which has since been prepared by Mayer and Oppenheimer (*Ber.*, 1918, **51**, 1239). The characteristics of this derivative as described by these authors do not coincide with those of any of Ekstrand's supposed nitronaphthoic acids.

Repetition of Ekstrand's experiments, using his second method of nitration (*i.e.*, in absence of any solvent), has shown that approximately equal amounts of 5- and 8-nitro-2-naphthoic acids are formed in at least 95% combined yield. Some low-melting indeterminate fractions of the esters resulting from the use of alcohol or benzene as crystallising medium were all easily resolved by employing ethyl acetate and light petroleum. With regard to Ekstrand's highest-melting ester (m. p. 131°) which charred with sulphuric acid, it is to be noted that the ethyl ester of 7-nitro-2-naphthoic acid (prepared by the present authors at a later stage) melts at 131°, but can be hydrolysed quite easily to give a quantitative yield of the nitro-acid. No trace of this ester was detected in the nitration product.

In addition to the 5- and 8-nitro-isomerides, we have succeeded in establishing the presence of traces of 1-nitro-2-naphthoic acid in the nitration mixture.* This acid cannot be esterified by the passage of hydrogen chloride into an alcoholic solution, and consequently was easily separated from the reaction material. It was never obtained quite pure, but reduction with ferrous sulphate and ammonia produced an aminonaphthoic acid, m. p. 202—205° (decomp.), the *acetyl* derivative of which crystallised from alcohol in long, gorse-like needles, m. p. 184°. This was identical with an authentic specimen of 1-acetylamino-2-naphthoic acid prepared synthetically (see Friedländer and Littner, *Ber.*, 1915, **48**, 330).

During the nitration of β-naphthoic acid, therefore, between 60—80° with excess of nitric acid (*d* 1·42) only 5-nitro-2-naphthoic acid (m. p. 291° instead of 288°) and 8-nitro-2-naphthoic acid

* Ekstrand (*ibid.*, 1890, **42**, 273) digested the mixture of nitro-acids with sodium hydroxide during an attempt to separate them by fractionation of their sodium salts. But Friedländer and Littner (*Ber.*, 1915, **48**, 330) have proved that hydrolysis of 1-nitro-2-naphthonitrile by alkaline reagents (even barium hydroxide) causes the replacement of the nitro-group by a hydroxyl group, and this also takes place in the case of the acid. It is therefore probable that Ekstrand had destroyed any 1-nitro-compound present.

(m. p. 295°) are formed in large quantity, together with a trace of 1-nitro-2-naphthoic acid.

Some New Amino- and Nitro-naphthoic Acids.

Of the seven theoretically possible amino-derivatives of α-naphthoic acid, only four (the 2-, 4-, 5-, and 8-amino-1-naphthoic acids) have hitherto been prepared. Even fewer of the nitro-α-naphthoic acids are known, since no compound containing one nitro-group in any of the four β-positions is recorded. Of the substituted derivatives of β-naphthoic acid, only one amino-acid, the 6-derivative, had not been prepared, but there were still four unknown nitro-isomerides, *viz.*, the 3-, 4-, 6- and 7-nitro-2-naphthoic acids.* As a result of the present work, 6- and 7-amino-1-naphthoic acids, 6-amino-, 6- and 7-nitro-2-naphthoic acids have been obtained for the first time.

The method adopted for the preparation of these aminonaphthoic acids consists in heating the neutral sodium salt of the corresponding hydroxynaphthoic acid† with ammonia and bisulphite under pressure. Möhlau and Kriebel (*Ber.*, 1895, **28**, 3096) had already employed strong ammonia (without bisulphite) to convert 3-hydroxy-2-naphthoic acid into the amino-acid. Repetition of their experiment, however, showed no appreciable conversion, either with the 3-isomeride or any other. Neither could the 3-amino-compound be obtained when bisulphite was used, though the conditions were varied over a wide range. β-Naphthylamine was the sole product of reaction, as it was also from the anilide of 3-hydroxy-2-naphthoic acid (naphthol A.S.). Similarly, 1-hydroxy-2-naphthoic acid yielded α-naphthylamine.

In addition to the new aminonaphthoic acids mentioned, 5- and 8-amino-2-naphthoic acids have also been prepared by the use of the bisulphite modification.

All the amino-2-naphthoic acids thus obtained were converted into nitronaphthoic acids by treatment of the diazotised product with copper powder and excess of sodium nitrite, as described by Veselý and Dvořak (*Bull. Soc. chim.*, 1922, **31**, 421; 1923, **33**, 319). The 5- and 8-nitro-2-naphthoic acids so prepared were used

* Mention is made (A., 1923, **124**, i, 119) of a nitronaphthoic acid, m. p. 225—227°, obtained by Ruzicka and Stoll (*Helv. Chim. Acta*, 1922, **5**, 923) as a by-product in the oxidation of 2-methyl-8-*iso*propylnaphthalene with dilute nitric acid, the main product being 2 : 8-naphthalenedicarboxylic acid. The nitronaphthoic acid in question is really a nitro-8-*iso*propyl-2-naphthoic acid; the abstract is somewhat misleading.

† For the details of preparation of the various hydroxynaphthoic acids see Butler, Royle, and Schedler (J., 1923, **123**, 1641, 1649).

to confirm the identity of the nitration products of β-naphthoic acid (see previous section).

Experimental.

Conversion of Hydroxy-acids into Amino-acids.—The hydroxynaphthoic acid (15 g.) is dissolved in water with the aid of sodium bicarbonate (6·3 g.); ammonia (100 c.c., *d* 0·88) is added, followed by a solution, saturated at 15°, of sulphur dioxide in water (25 c.c.). The whole is diluted with water (110 c.c.), and heated in an autoclave at 200—210° (pressure about 50 atmospheres) for 10 hours. The solution is boiled to drive off most of the ammonia, filtered, and slightly acidified by the gradual addition of acetic acid. Under these conditions 5- and 8-amino-2-naphthoic acids separate in a very satisfactory condition. With 6-amino-2-naphthoic acid (and to a less extent with 6- and 7-amino-1-naphthoic acids) it is advisable to add an excess of warm dilute hydrochloric acid to the acetic acid solution. After extraction with ether to remove impurities, the solution is concentrated and the amino-hydrochloride allowed to crystallise. The free acid is regenerated by dissolving in a small quantity of sodium carbonate solution and carefully neutralising with acetic acid. 7-Amino-2-naphthoic acid is best isolated through its difficultly soluble sodium salt, by the addition of sodium hydroxide to the autoclave liquor after removal of excess of ammonia. The yield in every case is almost theoretical.

The various aminonaphthoic acids differ but slightly from one another as regards their solubilities. They are easily soluble in alcohol or acetic acid, somewhat less easily soluble in ether, acetone or ethyl acetate, and very sparingly soluble in benzene.

6-*Amino*-1-*naphthoic acid* crystallises from alcohol in light brown aggregates, m. p. 203° (Found: C, 70·4; H, 4·8. $C_{11}H_9O_2N$ requires C, 70·6; H, 4·8%). The *hydrochloride* crystallises from water in clumps of needles, and the *acetyl* derivative from alcohol in white needles, m. p. 170—172°.

7-*Amino*-1-*naphthoic acid* crystallises from alcohol in light brown prisms, m. p. 223—224° (Found: C, 70·3; H, 5·0%). The *hydrochloride* separates from water in warty clusters of needles, and the *acetyl* derivative from alcohol in almost white needles, m. p. 229—230°.

6-*Amino*-2-*naphthoic acid* crystallises from dilute alcohol in very pale yellow needles, m. p. 225° * (Found: C, 70·8; H, 4·7%).

* Since this work was completed a compound described as "6-amino-2-naphthoic acid" has been obtained by Dziewoński, Schoenówna, and Waldmann (*Ber.*, 1925, **58**, 1211). These authors give the melting point as 222—223°; but the acetyl derivative, from which the free amino-acid

The *hydrochloride* is not very soluble in cold but rather more soluble in hot water, crystallising in small flakes. The *acetyl* derivative separates from dilute alcohol or from acetone in white needles, m. p. 230—232°.

7-Amino-2-naphthoic acid crystallises from alcohol in pale yellow leaflets, m. p. 245°. Its *acetyl* derivative separates from dilute alcohol in almost white, flat needles, m. p. 200—201° (decomp.).*

Types of Fluorescence shown.

Solvent.	α : 6-.	α : 7-.	β : 4-.	β : 5-.	β : 6-.	β : 7-	β : 8-.
Alcohol	Green	Emerald green	Blue	Green	Purple	Sea green	Emerald green
Ether	Light blue	Emerald green	Royal blue	Cobalt blue	Purple	Pale blue	Turquoise blue
Acetic acid	Pale violet	Bluish-green	(Blue)	(Green)	Cobalt blue	Bluish-purple	Leaf green
Benzene	Royal blue	Sky blue	Bluish-purple	Light blue	Violet blue	(Blue)	Greenish-blue
Ethyl acetate	Turquoise blue	Turquoise blue	Blue	Greenish-blue	Reddish-violet	Blue	Bluish-green
Acetone	Greenish-blue	Turquoise blue	Royal blue	Turquoise blue	Reddish-violet	Blue	Bluish-green

A few of these fluorescences require magnesium light or the light from an iron arc to render them visible; such are indicated by brackets. The majority are very marked, even in subdued daylight. The colours given in the table are those induced by arc light; they vary slightly in one or two instances from the fluorescences in daylight.

In addition to the preceding observations on the fluorescent properties of aminonaphthoic acids taken under approximately standard conditions, 1-amino-2-naphthoic acid furnishes an appreciable blue fluorescence in alcohol, ether, or acetic acid, while 3-amino-2-naphthoic acid (according to Möhlau and Kriebel, *loc. cit.*) gives a green fluorescence in alcohol or ether.

It is worthy of note that the aminonaphthoic acids whose configurations correspond to those of possible naphthaquinones produce more intensely fluorescent solutions than those not having a potentially quinonoid structure; *e.g.*, β : 8- is stronger than β : 5-; β : 6- than β : 7-; and α : 7- than α : 6-.

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was prepared, melts at 271—272°. It is to be observed that the configuration of this isomeride was only arrived at by a process of exclusion. On the other hand, the constants given do not coincide with those of any other amino-2-naphthoic acid, all of which are now known.

* It is important to carry out the melting-point determinations of these acetyl derivatives in a standardised manner, in order to ensure concordant results. No method other than the one here described gives a definite fluid melt. The tube is inserted when the temperature of the bath is only about 5° below the expected m. p. of the substance, and the time taken for the necessary rise in temperature must be less than 2 minutes. Incipient softening usually precedes liquefaction, and on increasing the temperature the substance reverts to the solid state, melting a second time, though not sharply, at a somewhat higher temperature. (To suggest that the m. p.—271—272°—recorded in the previous note is really this higher melting point would be somewhat premature, since the range is limited to 1°.)

Conversion of Amino-acids into Nitro-acids.—The aminonaphthoic acid (8 g.) is dissolved in warm glacial acetic acid (30 g.), and sulphuric acid (16 g.), diluted with an equal volume of water, added with constant stirring. The sulphate which separates is at once diazotised at 0° with sodium nitrite (3·5 g.) dissolved in water (15 c.c.). The clear diazo-solution is poured in small portions into a solution of sodium nitrite (35 g. in 140 c.c. of water) containing also clean copper bronze (30 g.). The reaction liquor, on standing at room temperature for 4 hours with regular shaking, deposits the whole of the nitronaphthoic acid, which is filtered off and purified by repeated extractions with boiling alcohol (charcoal). The filtered alcoholic solution is concentrated to a small bulk; the addition of water then precipitates the nitronaphthoic acid as a yellow powder. The total yield is about 0·5 g.

6-*Nitro*-2-*naphthoic acid* crystallises from alcohol in pale yellow plates, m. p. 310° (Found: C, 60·5; H, 3·4. $C_{11}H_7O_4N$ requires C, 60·8; H, 3·2%). The *ethyl* ester, m. p. 177°, crystallises in brownish-yellow, rectangular plates from ethyl acetate, in needles from alcohol. The acid can be recovered from the ester by hydrolysis with strong sulphuric acid on the water-bath for a few hours.

7-*Nitro*-2-*naphthoic acid* crystallises from alcohol in yellow needles, m. p. 262° (Found: C, 60·6; H, 3·4%). It is moderately soluble in acetic acid, but dissolves with difficulty in other solvents. The *ethyl* ester crystallises from alcohol in pale salmon-coloured, silky needles, m. p. 131°. This ester shows no sign of charring when hydrolysed with sulphuric acid in the usual way (compare Ekstrand's ester, m. p. 131°; see p. 85).

One of us (H. A. H.) desires to express his thanks to the Department of Scientific and Industrial Research for a maintenance grant, and to the Research Fund Committee of the Chemical Society for a grant for chemicals. We are also indebted to Professor Lapworth for his interest in the work.

THE UNIVERSITY, MANCHESTER. [*Received, November 24th*, 1925.]

XVII.—*A Revision of the Structural Formula of Glucose.*

By WILLIAM CHARLTON, WALTER NORMAN HAWORTH, and STANLEY PEAT.

THE discovery of the methylglucosides and the interpretation of the phenomena of mutarotation of sugars furnished the strongest reasons for the allocation of an oxide ring structure to the mono-

saccharides, and this formulation has been universally accepted. Tollens first ascribed to glucose a heterocyclic structure, and this conception was adopted by Fischer, who represented the normal methylglucosides by a five-membered or pentaphane ring, constituting the γ-oxide formula, which is the current and generally recognised basis for the formulation of sugars.

The methylglucosides were isolated in α- and β-stereochemical forms, and it was shown that corresponding to these there existed also α- and β-modifications of glucose. In 1914, Fischer (*Ber.*, **47**, 1980) prepared a new methylglucoside which differed profoundly in stability from the α- and β-modifications. This he described as "γ"-methylglucoside. The nomenclature he adopted seemed unfortunate inasmuch as in this case the Greek letter was not intended to have any stereochemical significance but merely represented a third or novel form. Fischer recognised that the new variety of methylglucoside was a structural isomeride, and thus the term γ-sugar introduced in this connexion had no essential relationship to the γ-lactones. Confusion has naturally arisen from the use of this terminology, and especially so since the term "γ-oxide form" was already applied to the normal sugars.

An experimental basis for the definite allocation to glucose of a γ-oxide (butylene oxide) constitution rather than that of any other oxide or heterocyclic structure was definitely lacking. Assuming, however, the spatial distribution of the oxygen valencies to be similar to those of carbon, and applying the considerations arising from the Baeyer strain theory, it was apprehended that a five-membered ring would involve the least strain in the sugar molecule, and this type of ring should, therefore, be capable of easy formation. It is tacitly assumed here that the conditions of strain in such a ring would be analogous to those in *cyclo*pentane, where the carbon atoms carry only hydrogen. These conditions seemed to be supported by the facility with which sugars give rise to lactones, and by the properties which the latter display suggesting their resemblance to γ-lactones. Kiliani and Kleemann (*Ber.*, 1884, **17**, 1300) attempted to obtain direct proof of the structure of gluconolactone, but it was left to Hudson to furnish, by his brilliant theoretical studies, the most convincing evidence of the γ-lactonic nature of the products of the oxidation of sugars.

In considering twenty-four lactones of the sugar series derived from the corresponding polyhydroxy-monobasic acids, Hudson (*J. Amer. Chem. Soc.*, 1910, **32**, 345) found that if it were postulated that ring formation occurred at the γ-carbon atom, a remarkable parallelism was exhibited between the position of the lactone ring

and the sign of the rotation of the lactone, and that there were no cases of disagreement on the basis of this hypothesis. On the other hand, it was demonstrated that if this linking occurred at the α-, β-, or δ-carbon atom, the number of cases of disagreement with this "rule" were found to be 8, 10, and 12, respectively, out of the twenty-four lactones examined. He calculated that, on the theory of probability, the chances are 17 millions to one that the lactone will have the lactonic ring engaging the γ-carbon atom. This conclusion is supported by an abundance of other cases, and in the absence of direct synthetic evidence to the contrary, this view of the constitution of lactones derived from unsubstituted sugars must be adopted.

It has, however, been too readily assumed that an analogy should be drawn between this principle of lactone ring formation and the type of ring structure existing in the parent sugars. In instituting the inquiry of which details are given in this communication, the present authors have attempted to test the validity of the latter assumption.

It was considered that there should be recognisable differences in stability between lactones of the usual γ-type and those having a smaller or larger number of atoms than five constituting the ring, and that these differences would be reflected in a variation both in the rate and in the extent of hydrolysis to the open-chain acid. During the past 4 years the necessary synthetic materials and the data for this comparison have been accumulated, and in recent communications some of these results have been recorded by one of us without reference, however, to their essential bearing on the present problem.

The degree of accuracy attainable by direct titration of aqueous solutions of the lactones was insufficient for the purpose indicated. A more sensitive method of comparison was provided by studying the polarimetric changes accompanying ring scission from lactone to open-chain acid, using either aqueous or alcohol–water solutions.

Polarimetric data furnished by the completely methylated lactones derived from glucose, galactose, mannose, arabinose, and xylose led to a recognition of two types. Those lactones prepared from the normal forms of these sugars, by first methylating the aldoses and then submitting them to oxidation with bromine water, exhibited a rapid diminution or increase in specific rotation when dissolved in water or aqueous alcohol. Conversely, those lactones prepared from the labile or γ-sugars displayed a very slow and much less marked change in specific rotation.

Observed Changes in the Specific Rotation of the Lactones from the following Sugars (aqueous solutions).

	γ-Forms (Time, 20 days).	Normal forms (Time, 24 hrs.).	Nos. of Curves.
Tetramethyl glucose ...	$+61{\cdot}5° \longrightarrow 39{\cdot}6°$	$+101{\cdot}1° \longrightarrow 25{\cdot}6°$	i and ii
Tetramethyl galactose	$-27{\cdot}1° \longrightarrow 25{\cdot}2°$	$+161{\cdot}5° \longrightarrow 27{\cdot}2°$	iii and iv
Trimethyl arabinose ...	$-42{\cdot}2° \longrightarrow 25{\cdot}1°$	$+145° \longrightarrow 22{\cdot}4°$ *	v and vi
Trimethyl xylose	$+74{\cdot}1° \longrightarrow 61{\cdot}4°$	$-3{\cdot}8° \rightarrow +20{\cdot}8°$	vii and viii
		(Time, 7 days)	
Tetramethyl mannose.	$+65{\cdot}2° \longrightarrow 56{\cdot}3°$†	$+105° \longrightarrow 45{\cdot}6°$	

* This value was determined by Pryde, Hirst, and Humphreys (J., 1925, **127**, 348).

† This figure is explained in the text, since it was obtained by Levene and Meyer from methylated mannonolactone. The time intervals are not recorded.

The curves given in Fig. 1 are those of the lactones related to glucose, galactose, and arabinose. Inspection of these curves suggests that the lactones represented by i, iii, and v are of the same type, and that those shown by ii, iv, and vi belong to a second and distinct type.

This second series illustrates the polarimetric data given by the lactones prepared from the normal forms of tetramethyl glucose, tetramethyl galactose and trimethyl arabinose, which exhibit a marked decline in specific rotation when dissolved in water. The equilibrium between the cyclic compound and open-chain acid is speedily reached and hydrolysis is also more nearly complete as revealed by direct titration at this stage.

On the other hand, the first series (Nos. i, iii, and v) represents lactones prepared from the labile or γ-sugars, and it is seen that the initial rotations are lower and that a much less profound change in the optical values occurs. Moreover, equilibrium between lactone and hydroxy-acid is only attained after several weeks, and at this stage hydrolysis is not nearly so complete as in the case of the former series.

The curves shown in Fig. 2 differ in a similar sense, but not in the same degree; the steeper of the two represents the lactone from normal trimethyl xylose, whilst the remaining curve, which is almost linear, is given by the lactone from trimethyl γ-xylose.

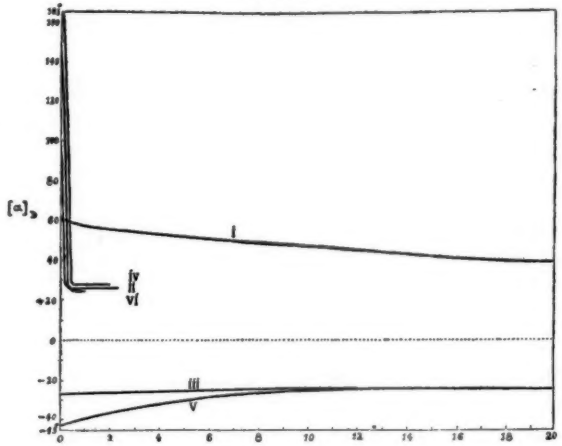
Fortunately, it is possible to correlate these data with constitutional formulæ which have been already determined for several of these sugars and their derived lactones, but for reasons which will be outlined later the constitution of the two glucoses and their gluconolactones had not yet admitted of any proof.

The method which is adopted in this communication shows that the data now recorded render it possible to reach a reasonable

conclusion as to the structure of glucose and its γ-derivatives by observing the analogy which is found to subsist between their lactones and those of the other sugars of known constitution.

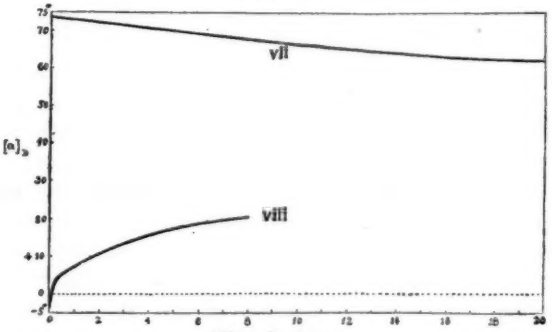
Of the four sugars examined (five, including mannose), two have been subjected to close constitutional study by direct methods

FIG. 1.



Time in days.

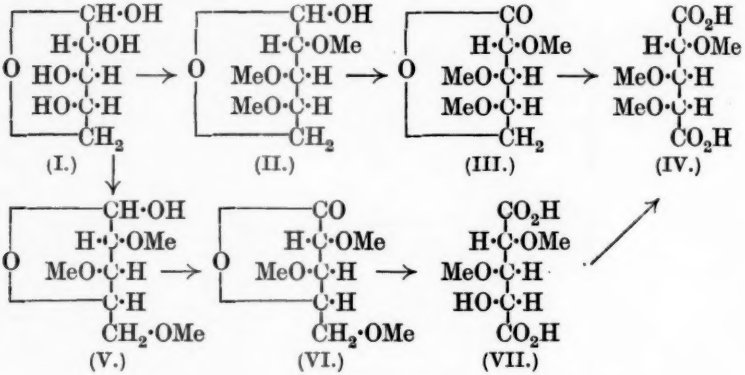
FIG. 2.

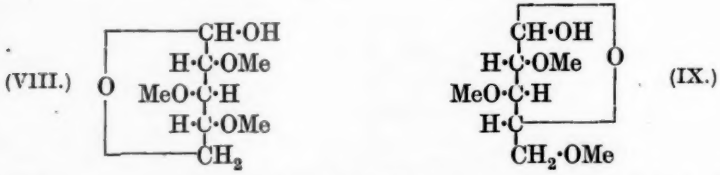


Time in days.

of oxidation. Thus Hirst and Robertson (J., 1925, **127**, 358) have demonstrated that the normal form of trimethyl *l*-arabinose must have the constitution (II), since it gives the dibasic acid (IV), namely, arabo-trimethoxyglutaric acid; and, since the properties of the trimethyl arabinose are in every respect similar to those of natural arabinose, the latter is given the constitution (I).

Another form of trimethyl arabinose was prepared by Baker and Haworth (J., 1925, **127**, 365), and this may be described as the "γ"-sugar. The formula (V) was allocated to this compound, since it gave rise to the lævorotatory lactone (VI) and, on further oxidation, to the dibasic acid (VII) which contained only two methoxyl residues. This latter, on complete methylation, was identical with Hirst and Robertson's acid (IV).



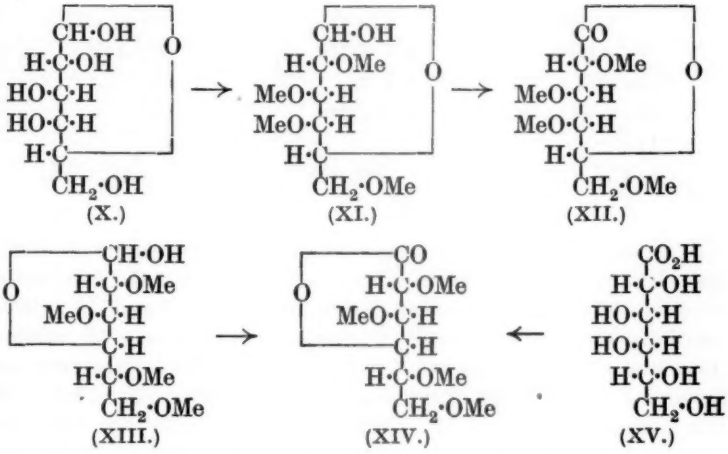


The same constitutional relationships have been established also for normal trimethyl xylose (VIII) (Hirst and Purves, J., 1923, **123**, 1352), which is found to give on oxidation the xylo-trimethoxyglutaric acid, stereoisomeric with the acid of formula (IV); and in a forthcoming paper by Haworth and Westgarth the preparation will be described of trimethyl γ-xylose, to which is allocated the structural formula (IX) analogous to that ascribed above (V) to trimethyl γ-arabinose.

Taking the two examples of the pentoses, xylose and arabinose, it is clear that the normal sugars are amylene-oxidic in structure, and that the labile or γ-forms are butylene oxides. The related lactones are therefore δ-lactones for the normal sugars and γ-lactones for the labile or γ-sugars.

Coming now to the case of galactose, it must be stated that the evidence as to structure depends here on Hudson's rule. Pryde (J., 1923, **123**, 1808) has shown that normal tetramethyl galactose (XI) changes to tetramethyl-δ-galactonolactone (XII) on oxidation,

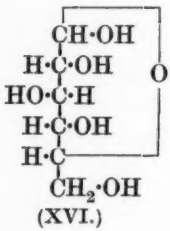
and therefore normal or naturally occurring galactose is given the constitution (X). The corresponding labile or γ-sugar (XIII) was prepared by Haworth, Ruell, and Westgarth (J., 1924, **125**, 2468) and this on oxidation gave rise to the γ-lactone (XIV), which is also obtained on passing from ordinary or normal galactose or from galactonic acid (XV) to its lactone. The rotations of the compounds resulting from all these transformations are completely in accord with Hudson's rule, which, it may be emphasised, requires that galactonolactone must be a γ-lactone (see p. 90).

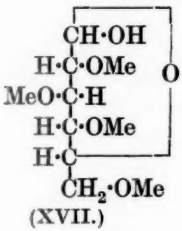


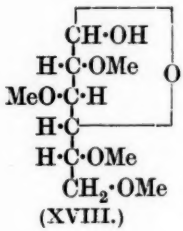
Similarly, mannose has been shown to conform to the above structural scheme. Levene and Meyer (*J. Biol. Chem.*, 1924, **60**, 167) found that normal tetramethyl mannose gave a lactone, $[\alpha]_D + 105° \longrightarrow 45{\cdot}6°$, whilst methylation of the lactone from mannonic acid led to the isolation of a different and crystalline tetramethyl mannonolactone having $[\alpha]_D + 65{\cdot}2° \longrightarrow 56{\cdot}3°$. These optical values will be found to be closely similar to those quoted later for δ- and γ-lactones, respectively, but as the authors did not record the intermediate rotation values at short period intervals the curves could not be included in Figs. 1 and 2.

It only remains, therefore, to apply this analogy to the lactone from normal tetramethyl glucose, which is indicated by the remaining curve (ii) in this series. This conforms definitely to the same type as the other three (Nos. iv, vi, and viii), and we therefore regard it as a δ-lactone, and the normal tetramethyl glucose is therefore considered to be amylene-oxidic and consequently we assign to it the structural formula (XVII), whence glucose has the formula (XVI).

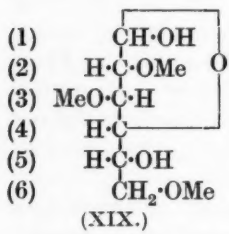
The other curves in Figs. 1 and 2, Nos. i, iii, v, and vii, clearly belong to a different category from those already discussed. All these represent the lactones prepared from the methylated "γ"-sugars. We have demonstrated that, since three of the four substances are γ-lactones, the sugars from which they are prepared are butylene-oxidic in structure, and by analogy the curve No. i is considered to be that of tetramethyl γ-gluconolactone, whence it follows that tetramethyl γ-glucose should be given the constitution (XVIII).

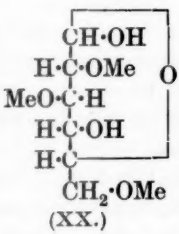

(XVI.)

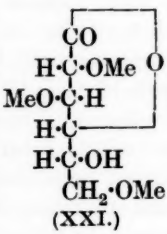

(XVII.)

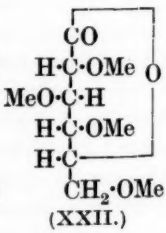

(XVIII.)

A second line of argument as to the constitution of glucose is provided by evidence drawn from the study of 2 : 3 : 6-trimethyl glucose. This sugar has been repeatedly examined and the relative positions of its three methyl groups are definitely determined (Denham and Woodhouse, J., 1914, **105**, 2361; Haworth and Leitch, J., 1918, **113**, 191; Haworth and Hirst, J., 1921, **119**, 193; Irvine and Hirst, J., 1922, **121**, 1213). We are concerned only with the ring structure of this compound, which, if the argument already presented in this paper be accepted, should now be revised from that indicated by formula (XIX) to the new formula (XX).


(XIX.)


(XX.)


(XXI.)


(XXII.)

Now it is known (Haworth and Hirst, *loc. cit.*) that the sugar is converted on further methylation into normal tetramethyl glucose and earlier in this paper the structural formula (XVII) has been ascribed to the latter on the ground that the derived lactone is a δ-lactone (XXII).

Inspection of the two alternative formulæ (XIX and XX) sug-

gests, however, a possible application of this sugar as a means of testing the validity of this reasoning and of the conclusions already drawn. Thus this sugar on oxidation to the monobasic acid offers a choice of two free hydroxyl positions for the attachment of the lactone ring, namely, those on carbon atoms (4) and (5) (formula XXI), and this applies no matter which of the two sugar formulæ is the correct one.

Adopting Hudson's rule, this choice must be restricted to that of the γ-lactone (XXI). If now this trimethyl γ-gluconolactone should, on complete methylation, be shown to be identical with that tetramethyl gluconolactone derived from normal tetramethyl glucose, then the latter sugar (and therefore glucose also) would be butylene-oxidic in structure and the formula hitherto generally accepted for glucose would continue to hold.

In the actual event this was found not to be the case; it was observed that 2 : 3 : 6-trimethyl glucose gave a gluconolactone (XXI) which on methylation was identical with the tetramethyl γ-gluconolactone derived from the labile or γ-form of tetramethyl glucose (XVIII), and therefore the constitutional formula for the latter is substantiated, and fresh support is provided for the argument outlined in the former part of this communication.

Moreover, the crystalline phenylhydrazides of the tetramethyl gluconolactones from the three sources were prepared and analysed, and the following are the data for the melting points:

Phenylhydrazides of tetramethyl gluconolactones.

	M. p.	Mixed m. p. with (*c*).
(*a*) From normal tetramethyl glucose	109—112°	102—118°
(*b*) From tetramethyl γ-glucose	131—134	130—133
(*c*) From 2 : 3 : 6-trimethyl glucose	130—133	

Thus we again reach the conclusion that ordinary glucose should be given the formula (XVI). This assumes that ordinary free glucose is identical in structure with normal tetramethyl glucose, but this is shown to be the case because α- and β-methylglucosides give crystalline tetramethyl glucose on methylation followed by hydrolysis, as do those natural di-, tri-, and poly-saccharides which contain the glucose residue, and moreover, E. F. Armstrong has shown that α- and β-glucose are stereochemically parallel to α- and β-methylglucosides.

All the commonly occurring aldoses are therefore shown to exist normally as amylene- or 1, 5-oxide forms, or, reverting to the older nomenclature which we prefer, they may now be described as δ-oxides. So far this has been shown to apply to glucose,

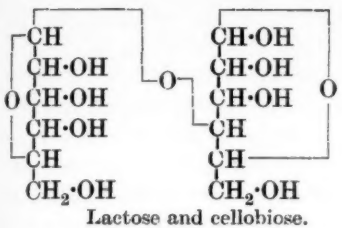
galactose, mannose, arabinose, and xylose. By a curious coincidence the so-called "γ"-sugars of the aldose type, which have now been shown to give rise to γ-lactones, may be more accurately described as γ-oxides, since they exist as butylene- or 1 : 4-oxide forms.

There remain to be mentioned the ketoses, and the constitutional study here has been confined to fructose, which occurs naturally as a γ-form in sucrose, raffinose, and inulin. The results of oxidation experiments conducted on tetramethyl γ-fructose derived from sucrose indicate that, in this sugar, an amylene- or δ-oxide ring is present (Haworth and Linnell, Haworth and Mitchell, J., 1923, **123**, 294, 301). On the other hand, Irvine and Patterson (J., 1922, **121**, 2696) have examined the constitution of the normal form of tetramethyl fructose, which is crystalline, and which has not yet been isolated from a naturally occurring carbohydrate. This sugar they found to have the structure of a butylene- or γ-oxide. Thus, in the series of the ketoses, the position as compared with the aldoses would seem to be reversed, in that the labile sugar is the δ-oxide form, and the normal sugar the γ-oxide. It would therefore appear that, in nature, both aldoses and ketoses occur as amylene- or δ-oxides, a result which is in keeping with the simplest view of the synthesis of sucrose in the plant.

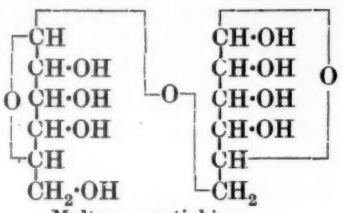
If this revision of the structural formula of glucose be accepted and applied to other carbohydrates, many fundamental readjustments are rendered necessary. Thus the constitutional formulæ allocated to natural di- and tri-saccharides by one of the present authors are directly implicated, as are also those suggested for starch and cellulose by other workers. These compounds will now require to be formulated as possessing δ-oxide rings in each hexose residue. In the case of lactose and cellobiose this change also involves a displacement of the point of attachment of the hexose chains from a position associated with the fifth carbon atom to that of the fourth.*

Leaving out of account the stereochemical relationships, it is now possible to represent the principal disaccharides by three formulæ :

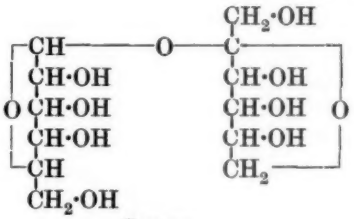
* It is, however, possible to regard one glucose residue in each of these disaccharides as existing as a γ-oxide or γ-sugar, in which case the earlier constitution will continue to hold with respect to the position of the biose linking, but this is an unlikely contingency. That 2 : 3 : 6-trimethyl glucose can pass into a γ-oxide form is extremely probable, and indeed we have some evidence of this. It is important to notice, however, that the sugar 2 : 3 : 5-trimethyl glucose must now be regarded as 2 : 3 : 4-trimethyl glucose, and that normal crystalline tetramethyl glucose is now 2 : 3 : 4 : 6-tetramethyl glucose.



Lactose and cellobiose.



Maltose, gentiobiose (amygdalin-biose) and melibiose.



Sucrose.

EXPERIMENTAL.

Tetramethyl δ-Gluconolactone.—This lactone was prepared by oxidising normal crystalline tetramethyl glucose with bromine water under the usual conditions (Purdie and Irvine, J., 1903, **83**, 1021). It was then dissolved in a slight deficiency of $N/10$-sodium hydroxide, and the aqueous solution evaporated at 35—40° under diminished pressure. The residue of sodium tetramethyl gluconate was triturated thrice with dry chloroform to remove traces of unoxidised sugar and other impurities and the remaining solid was filtered, washed with chloroform, dried, and weighed. An aqueous solution of the salt was then decomposed by adding the equivalent of dilute hydrochloric acid from a burette. Isolation of the purified lactone was effected by evaporation under diminished pressure, followed by extraction from the semi-solid residue with dry ether. The tetramethyl δ-gluconolactone distilled completely at about 100°/0·05 mm. and showed n_D 1·4532. *Titration.* 0·1355 g. required 6·05 c.c of 0·0965N-NaOH (Calc., 6·02 c.c.).

A titration was also conducted after keeping an aqueous solution of the lactone for 24 hours; it then appeared that more than 90% had been converted into the open-chain acid.

Determinations of the rotation of the lactone were recorded as follows:

In ethyl alcohol ($c = 3·65$), $[\alpha]_D + 101·1°$.

In aqueous alcohol (38% EtOH) ($c = 1·39$):

Time in hours .	0·25	2	5	21	25	66	
$[\alpha]_D$	+90·3°	84·0°	68·0°	40·7°	38·4°	38·4°	constant

In water ($c = 1{\cdot}37$) :

Time in hours .	0·1	3	5	6·5	8·25	26·25	
$[\alpha]_D$	+88·5°	43·2°	31·4°	25·6°	25·6°	25·6°	constant

Phenylhydrazide Derivative.—This was obtained by heating for 3 hours at 100° phenylhydrazine (1 mol.) with the above lactone (1 mol.). The crystals which appeared on cooling were recrystallised from ether and light petroleum and melted at 109—112°. On admixture with the phenylhydrazide of the γ-lactone as prepared below under (A) and (B), (m. p. 130—133°) the melting point for the mixture was depressed to 102—118° (Found : C, 56·1; H, 7·6; N, 8·0. $C_{16}H_{26}O_6N_2$ requires C, 56·1; H, 7·6; N, 8·2%).

Tetramethyl γ-Gluconolactone.—(A) In one experiment, 4·3 g. of 2 : 3 : 6-trimethyl glucose were oxidised with bromine water and the corresponding lactone was isolated in the usual way. This product was purified by extraction with light petroleum, which dissolved the lactone, leaving as residue traces of unchanged sugar. *Titration.* 0·0943 g. required 4·24 c.c. of N/10-NaOH (Calc., 4·48 c.c.) (Found : OMe, 40·9. Calc., OMe, 42·2%).

The tetramethyl gluconolactone was obtained by twice methylating the above product with Purdie's reagents and was thereafter distilled. It showed n_D 1·4470 (Found : C, 51·6; H, 7·8; OMe, 53·5. Calc., C, 51·3; H, 7·7; OMe, 53·0%). *Titration.* 0·0945 g. required 3·86 c.c. of N/10-NaOH (Calc., 4·03 c.c.).

In a second experiment, using a highly purified specimen of 2 : 3 : 6-trimethyl glucose, the tetramethyl γ-gluconolactone distilled at 92—96°/0·02 mm. and the colourless liquid was dissolved in a slight excess of aqueous barium hydroxide, left over-night, and then heated at 70° for 1 hour. Thereafter the excess of barium hydroxide was precipitated by admitting carbon dioxide, the filtrate evaporated under diminished pressure, and the residue extracted with ether to remove impurities. Solution of the barium salt in water containing the requisite equivalent of hydrochloric acid led to the isolation of the purified γ-lactone, which showed $[\alpha]_D = +49{\cdot}7°$ in ethyl alcohol ($c = 2$), and on dilution with water (44%) this value changed in 3 hours to +48·9°, and thereafter showed little change during 2 days. A titration showed that at this stage about 30% of the lactone had been converted into the acid.

The phenylhydrazide was prepared by adopting the same procedure as that described below. The product was washed with petroleum, and recrystallised from ether. M. p. 130—133° (Found : C, 56·05; H, 7·8; N, 8·2. Calc. for $C_{16}H_{26}O_6N_2$, C, 56·1; H, 7·6; N, 8·2%).

(B) The above lactone was also prepared from tetramethyl γ-glucose (Irvine, Fyfe, and Hogg, J., 1915, **107**, 529), the precaution being taken to separate any traces of the normal sugar

by the method of hydrolysing the methylglucoside with $N/15$-hydrochloric acid, since acid of this concentration has little effect on the normal glucosides but effects the complete hydrolysis of the γ-form. The γ-sugar was oxidised with bromine water in the usual way, and the above lactone distilled as a colourless liquid, b. p. 97°/0·05 mm., n_D 1·4467. In ethyl alcohol ($c = 2·07$) the specific rotation was + 53·7°, and on dilution with water (44%) the reading was $[\alpha]_D = +49·8°$, falling to 48·9° in 4 hours, at which value it remained constant for 2 days.

The polarimetric data were recorded for an aqueous solution of the lactone.

Time in hours ...	0·16	1·33	5·06	19·33	43·83
$[\alpha]_D$	+61·5°	60·7°	57·2°	56·2°	55·6°
Time in days	6	7	12	15	20
$[\alpha]_D$	+48°	47·4°	44·0°	39·6°	39·6°

Phenylhydrazide.—The lactone was heated during 3 hours at 100° with an equivalent proportion of phenylhydrazine. The product had crystallised during this period, and the crystals were purified from light petroleum and dry ether. M. p. 131—134°. In admixture with the specimen of the phenylhydrazide prepared as described above (A) there was no depression of the melting point (Found: C, 56·2; H, 7·8; N, 8·2%).

Tetramethyl δ-Galactonolactone.—The specimen prepared by Haworth, Ruell, and Westgarth (*loc. cit.*) was purified and used in the following determinations of specific rotations in water ($c = 0·95$):

Time in mins. ...	19	40	79	100	165	220	280	340
$[\alpha]_D$	+161·1°	146·3°	122·1°	98·9°	62·1°	46·3°	36·8°	32·6°
Time in hours ...	7	8	10	22	46			
$[\alpha]_D$	28·4°	28·2°	27·4°	27·2°	27·2°			

Trimethyl γ-Arabonolactone.—The crystalline specimen used was that prepared by Baker and Haworth (*loc. cit.*). The solvent was water.

Time in days	0	4	10	20
$[\alpha]_D$	−42·0°	33·8°	26·0°	25·1°

Other optical data employed in constructing the curves given in the introduction will be found by consulting the references quoted.

The authors express their indebtedness to the Department of Scientific and Industrial Research for maintenance grants and to the Armstrong College Research Endowment Fund for financial assistance.

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XVIII.—*Studies in Adsorption by an Optical Method. Fixation by Dispersoids of Methylene-blue within the Disperse Phase.*

By Andor Fodor and Rassa Riwlin.

Adsorbents in a comparatively coarse state of division, and therefore readily separable from the solution, have hitherto been used in investigations on adsorption. When one comes to deal with colloidal, finely divided adsorbents—and there is no doubt that the micelle of a sol also can act as an adsorbent—the difficulty of separating the phases from one another becomes almost insurmountable. Scarcely any case of this kind has been thoroughly examined because of the experimental difficulties. Dynamic methods, which cause a displacement of the equilibrium, and ultrafiltration are useless. The applicable static methods are limited in number. Potentiometric and conductivity methods, useful as they are in the case of proteins, which adsorb relatively large quantities of electrolytes, can be employed to measure the adsorption of only a few definite ions, and the method of compensation-dialysis has many disadvantages, one of which is the disturbance due to the membrane. For these and other reasons, it seemed to the authors that an optical method would be the most suitable for measuring adsorption, and, since the polarimeter and the refractometer cannot deal with opaque or turbid liquids, it should be based upon the absorption of light.

The concentration of a dye in solution will diminish on addition of a colloidal solution, owing to adsorption of the dye by the micelle. The absorption curves of the dye solution before and after the addition will therefore not be the same; and the difference between them will be a measure of the adsorption, if other losses of light, *e.g.*, by diffusion, do not affect the result.

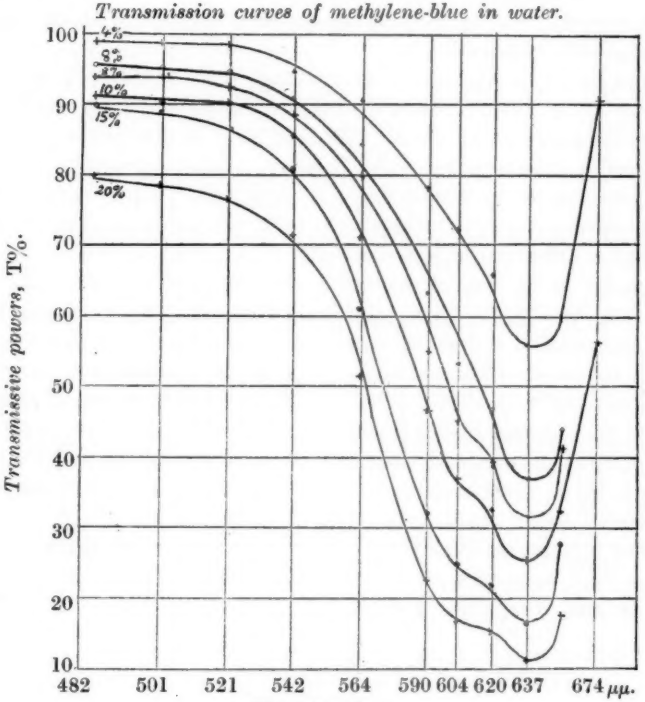
A suitable dye solution must comply with the following requirements: 1. It must be stable. 2. Its absorption spectrum must (*a*) fall within the visual region and not be too extended, and (*b*) be continuous and consist of one band. The curve will then have only one maximum or minimum, in the neighbourhood of which slight changes can be very conveniently measured.

Method.—The transmissive powers, T, of a dye solution for light of different wave-lengths were measured directly in percentages with Vierorat's improved form of the Schmidt-Haensch spectrophotometer. The transmission curve of the solution was then obtained by plotting the values of T as ordinates and wave-lengths (λ) as abscissæ (Fig. 1).

The concentration of a dye solution may be determined by this method in the following way, which obviates the application of Beer's law. The absorption curves of a series of solutions of the dye of known concentrations are drawn. The minima of these curves will all lie on one and the same ordinate, *viz.*, that drawn through the wave-length corresponding to minimum transmissive power. A second graph is drawn, having the concentrations of the

FIG. 1.

Transmission curves of methylene-blue in water.



solutions as abscissæ and the corresponding minimal transmissive powers as ordinates. The minimal transmissive power of the solution of unknown concentration is now determined from its transmission curve, and the corresponding abscissa in the second graph will then give the concentration.

EXPERIMENTAL.

Preparation of the Dye Solutions.—A series of solutions was prepared containing 4, 6, 8, 10, 12½, 15, 17½, 20, 25, 30, 40, and 50% *

* For convenience' sake, a true concentration of 0·000n% is written as n%.

of a standard solution of methylene-blue (0·1 g. in 1000 c.c. of water). Ten c.c. of each of those solutions were mixed with 10 c.c. of water, and the transmission curves of the mixtures were plotted (Fig. 1). From time to time, the transmissive powers were redetermined to ensure that they still agreed with those of the freshly prepared solutions, and therefore that the concentrations of methylene-blue were unchanged.

Methylene-blue is adsorbed by many substances, including filter-paper. The solutions, therefore, were not filtered and the parts of the vessels used that would come into contact with the liquid were specially polished.

Solutions of methylene-blue are not very stable. Under the influence of light and air they slowly lose their colour, and much more quickly in presence of alkali. The mixture of methylene-blue and a sol under investigation was therefore compared with a solution having the same hydrogen-ion concentration. Wherever possible, for the preparation of the comparison liquid the same acid or alkali was used as that present in the sol.

In many cases the sol itself was cloudy. The effect of the consequent scattering of light was ascertained in the following way. The transmissive power (a) of a mixture of 10 c.c. of the sol with 10 c.c. of water was measured. If c is the transmissive power of the methylene-blue solution (10 c.c. of the diluted standard solution + 10 c.c. of water) and b that of the experimental mixture (10 c.c. of the diluted standard solution of methylene-blue + 10 c.c. of the sol), then, provided that there was no interference due to chemical reaction or adsorption, for each wave-length, $ac = b$.

If the sol transmitted light to the same extent as water, $a = 1$; and to find any deviation from the 'mixture' law, it was only necessary to compare c with b.

TABLE I.

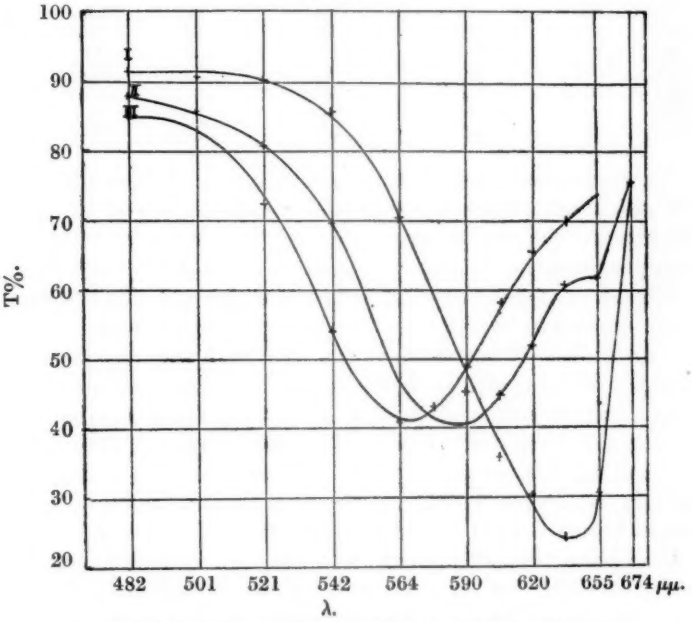
Transmissive powers of methylene-blue + silica sol.

	% Conc. of methylene-blue.						
λ (μμ).	4.	6.	8.	10.	12·5.	15.	17·5.
482	95	93	89·5	87·5	85	83	80
501	95·5	92·5	89	85·5	83	80	75
521	94	89·5	84·5	81	79	75	69·5
542	84	79·5	74·5	69	64	58	52
564	70	60	53	45	40	35	30
590	*65·5*	*55*	*47·5*	*40*	*34·5*	*25*	*22*
604	74·5	61	53·5	44·5	40	30	26·5
620	80·5	69·5	60	51·5	45·5	40	35
637	85	77	68	60	55	46	42
655	86	79	70	61	57·5	49	44
674	90	85	82	75	—	65	—

1. *Silica Sol.*—This was prepared by Ostwald's method ("Kleines Praktikum der Kolloidchemie," 3rd ed., p. 8, expt. 23). $a = 1$ for all wave-lengths.

The transmissive power of the reddish-violet mixture of the methylene-blue solution with the silica sol (Fig. 2, curve II) is quite different from that of its blue mixture with water (curve I); the minimum has shifted from λ 637 μμ to λ 590 μμ and is of about twice the magnitude. Moreover, the two transmission curves have

FIG. 2.



I, *Methylene-blue+water.* II, *Methylene-blue+silica sol.*
III, *Methylene-blue+silica sol+sodium hydroxide.*

different forms. These facts all indicate the production of a compound.

To prove that the effect of the sol on the methylene-blue was not due to the presence of hydrogen- or hydroxyl-ions, the transmission curves were determined of methylene-blue solutions containing these ions. It will be seen (Table II) that the addition neither of acid nor of alkali caused any considerable alteration in the position of the minimum of the curve for the methylene-blue solution during the time of observation. If the solutions were kept for some time, the minimum shifted towards the blue end of the spectrum (see last two columns). Acid was without appreciable effect

TABLE II.

Effect of acid or alkali on the transmissive powers of methylene-blue.

	12·5% Methylene-blue.			17·5% Methylene-blue + N/10-NaOH.		
λ (μμ).	+ Water.	+ N/10-HCl.	+ N/10-NaOH.	Soon after mixing.	After 2 hrs.	After 24 hrs.
482	91·5	91	90·5	79	79	61·5
501	92	91·5	89·5	75	75	55
521	91·5	90	89·5	69	67·5	45
542	85	85	83	55	55	35
564	70	68·5	70	40	39·5	29·5
590	46	39·5	51	29	29	*25*
604	36	30	41	25·5	*25*	48·5
620	31·5	25	35·5	24·5	25·5	65
637	*25·5*	*20*	*29·5*	*23·5*	29	75
655	32	26	35	28·5	37·5	80

on the transmissive power of the mixture of methylene-blue solution and silica sol, whilst the addition of alkali caused the point of inflexion in the region of $\lambda = 637$ μμ (Fig. 2, curve II) almost to disappear and the minimum to shift to $\lambda = 564$ μμ (curve III).

When a mixture of methylene-blue solution and silica sol was kept in an unpolished vessel, there was little if any adsorption of the dye on the walls. It seems as if the dye is so strongly held by the particles of sol that it is indifferent to any other influence.

An experiment with kaolin gave somewhat similar results: Mixtures of 10% methylene-blue solution with (*a*) water, (*b*) silica sol, and (*c*) 1% sodium silicate solution were each shaken with 100 mg. of kaolin, which was then allowed to settle. The supernatant liquid was (*a*) colourless, (*b*) violet-blue, (*c*) blue.

In another experiment, 2, 3, 5, 10, 30, and 50% solutions of methylene-blue were each mixed with 10 c.c. of silica sol and shaken with 100 mg. of kaolin. After settling, the sediment was coloured in every case, the liquors from the 2% and 3% solutions were colourless, and the others were slightly coloured.

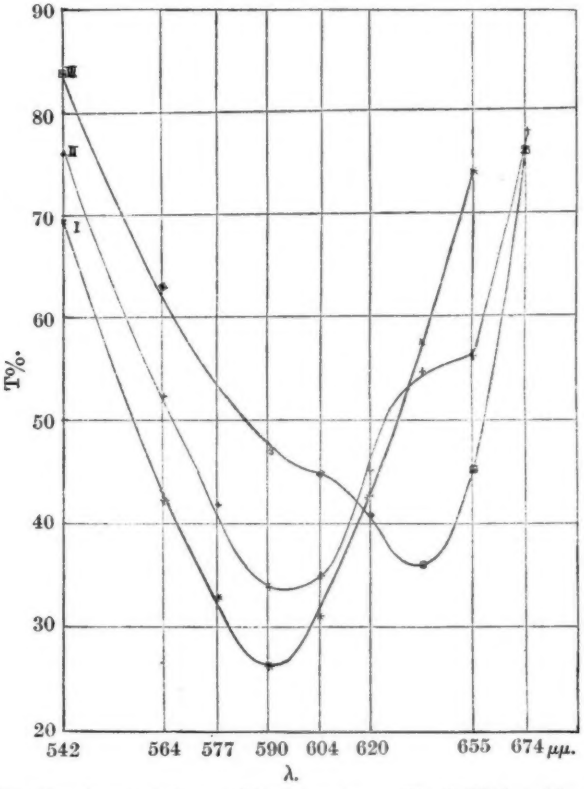
Sodium Silicate (Merck's commercial solution).—When the last experiment was repeated with a 1% solution of sodium silicate instead of the silica sol, even the liquors from the 2% and 3% solutions of methylene-blue were coloured. Sodium silicate seems to retain the dye better than silica sol.

On mixing solutions of methylene-blue and sodium silicate a blue precipitate was obtained or not according as the former or the latter was in excess. A similar behaviour was not observed in the case of the silica sol.

The transmission curves of mixtures of solutions of methylene-blue and sodium silicate were determined; the solutions were of

course alkaline. As in the case of the silica sol (Fig. 2, curve II), a minimum was found at λ 590 μμ (Fig. 3, curve I). On addition of insufficient hydrochloric acid for neutralisation the minimum was slightly displaced and a bend appeared in the region of λ 637 μμ (curve II). When the mixture was made acid, the minimum shifted to λ 637 μμ, its place being taken by a slight bend (curve III). If the

FIG. 3.



I, *Methylene-blue+sodium silicate+water.* II, *Methylene-blue+sodium silicate+hydrochloric acid (still faintly alkaline).* III, *Methylene-blue+sodium silicate+hydrochloric acid (faintly acid).*

acid was added very carefully until the mixture was neutral, the whole mass coagulated.

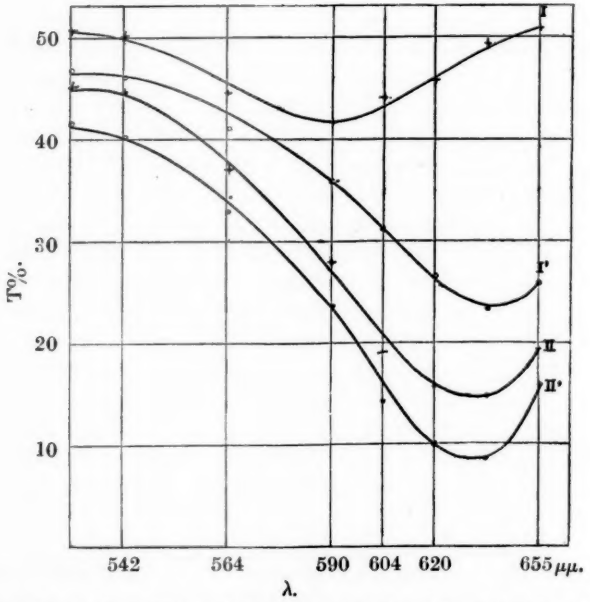
Kaolin.—A suspension of 2 g. of kaolin in 100 c.c. of water was kept for 18 hours, and the turbid liquor was then syphoned off. This liquor, containing only the finest particles of the kaolin, was used in the following experiments and was well shaken before each determination.

TABLE III.

Transmissive powers of mixtures of methylene-blue and kaolin.

	Me-b (6%) + kaolin.			Me-b (10%) + kaolin.			Me-b (15%) + kaolin.		
λ (μμ).	*a.*	*ac.*	*b.*	*a.*	*ac.*	*b.*	*a.*	*ac.*	*b.*
482	48	46	50	50	46	49	47	42	45·5
501	47·5	45·5	50·5	49·5	45·5	49	47	42	46
521	48·5	46	50·5	49	44	49	48·5	41·5	45
542	51	46	50	51	44·5	48	50	40	44·5
564	51·5	42	45	52	38	42·5	53·5	33	37·5
590	57	36	41·5	58	26	37	54·5	18	22
604	58	30·5	44	59	21	36	55	14	19·5
620	60	27	45·5	61	18	35	57	11·5	17
637	63	23·5	49	62	15·5	35	60	9	15
655	63	27	50·5	64	19	39	60	16·5	20

FIG. 4.



I=b *for the mixture* 6% *methylene-blue+kaolin.* I'=ac *for the mixture* 6% *methylene-blue+kaolin.* II=b *for the mixture* 15% *methylene-blue+kaolin.* II'=ac *for the mixture* 15% *methylene-blue+kaolin.*

The transmissive powers of the kaolin suspension (*a*), of the methylene-blue solution (*c*), and of the mixture of the two (*b*) were determined and *b* was compared with *ac* (Table III and Fig. 4). The *b* transmission curves and the calculated *ac* curves are almost parallel for the more concentrated solutions of methylene-blue, but diverge in the case of dilute solutions. The *b* curve, however, invariably lies above the corresponding *ac* curve, and therefore it

TABLE IV.

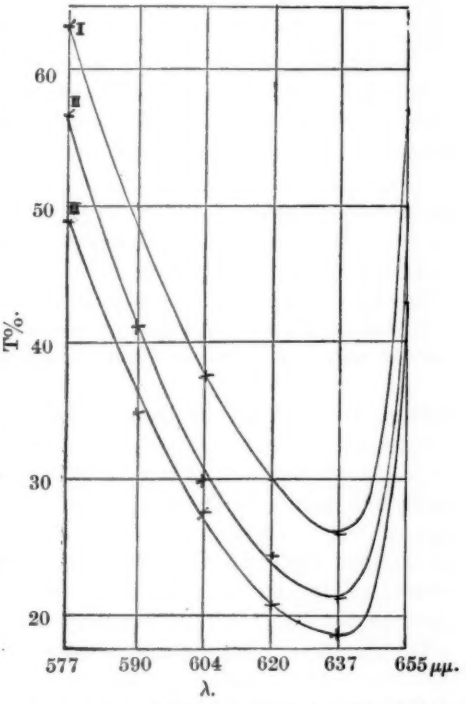
Transmissive power of methylene-blue (10%).

λ ($\mu\mu$).	+ Water	+ N/50-Acetic acid.	+ Aluminium hydroxide sol.
577	63	57	49
590	50	41	35
604	37·5	30	28
620	30	24·5	21
637	*26*	*21*	*18·5*
655	57	50	42·5

may be concluded that the methylene-blue is partly adsorbed by the kaolin.

Aluminium Hydroxide Sol.—The sol was prepared by Ostwald's method (*op. cit.*, p. 12, expt. 30). A mixture of methylene-blue solution and the sol was less transparent than the corresponding mixture of methylene-blue and water. This result was due to the presence in the sol of acetate ions, which diminish the transmissive power of methylene-blue (Table IV and Fig. 5). Almost identical transmission curves were obtained for the methylene-blue solution + the aluminium hydroxide sol and methylene-blue solution + an acetate buffer the p_H of which was the same as that of the sol (3·84).* No adsorption of methylene-blue, therefore, can be demonstrated in the case of aluminium hydroxide sol.

FIG. 5.



I, 10% *methylene-blue+water*. II, 10% *methylene-blue+N/50-acetic acid*. III, 10% *methylene-blue+aluminium hydroxide sol.*

Natural Protein.—A solution of white of egg in water (20 vols.)

* Compare A. Fodor, "Determination of the affinity constants of weak acids and bases" ("Handbuch der biologischen Arbeitsmethoden," E. Abderhalden, p. 474).

was filtered. The filtrate was turbid, and therefore *a* had to be determined. On comparing *ac* (where *c* = transmissive power of methylene-blue + buffer solution) with *b*, no difference was observed (Table V). Natural protein, therefore, does not adsorb methylene-blue.

TABLE V.

Transmissive power of white of egg + methylene-blue (10%).

λ (μμ).	*a*.	*c*.	*ac*.	*b*.	λ (μμ).	*a*.	*c*.	*ac*.	*b*.
482	92	93	85·5	86	590	95	47·5	45	44
501	93·5	93	87	86	604	95	35	33	34
521	93·5	92·5	86·5	85·5	620	95	29	27·5	28·5
542	94	84·5	79·5	78	637	95·5	24	23	24
564	95	70·5	67	69·5	655	96	33·5	32	34·5

An experiment was also made with the protein at the isoelectric point. Acid was added in increasing quantities to solutions of the protein, and the concentration was thus found (*viz.*, 0·6 c.c. of *N*/10-hydrochloric acid for 10 c.c. of protein solution) at which the protein coagulated most rapidly on heating. The above experiments were repeated with such a protein mixture, but again there was no difference between *ac* and *b*.

Finally, the protein was finely dispersed by the addition of sodium hydroxide (1 c.c. of *N*/10-solution to 10 c.c. of protein solution), and the mixture with methylene-blue examined in the usual way, the comparison liquid being a solution of sodium hydroxide of the same p_H as the protein mixture. No adsorption of methylene-blue was detected.

Casein.—A solution of 2 g. of casein (Hammersten) in 60 c.c. of water and 2 c.c. of *N*-sodium hydroxide was diluted to 100 c.c. with water, a slight excess of hydrochloric acid added, and the solution kept for 12 hours. The precipitated casein was washed free from chloride, and dissolved in 100 c.c. of *M*/15-disodium hydrogen phosphate or *M*/15-sodium carbonate.

The p_H of the phosphate solution was 7·45. A buffer solution of the same p_H was made by mixing 84 c.c. of *M*/15-disodium hydrogen phosphate with 16 c.c. of water.

Mixtures of either solution of casein (phosphate or carbonate) with methylene-blue were examined, but no difference was found between *ac* and *b*, and therefore no adsorption occurred.

Pure Albumin.—A 10% solution of white of egg was mixed with an equal volume of saturated ammonium sulphate solution, the precipitated globulin removed, and the filtrate dialysed for several days until it was free from sulphate. The solution of albumin thus obtained was used in experiments with methylene-blue, but no adsorption was detected.

Saponin.—The transmission curve of a mixture of methylene-blue with a 10% solution of saponin (for which $a = 1$) was the same as that of its mixture with water. There was, therefore, no adsorption.

Kobert (Freundlich, "Kapillarchemie," 3rd ed., 1923, p. 889) dialysed a saponin solution against a solution of methylene-blue and showed that the dye accumulated in the sol so that its concentration there exceeded that in the external solution. We tried to repeat this experiment; but the whole of the methylene-blue was adsorbed by our dialysis membrane ("Dialysierhülse" of Schleicher and Schüll) and both liquids became colourless.

Gelatin.—A 1% solution of gelatin, made by warming 1 g. to 70° with 100 g. of water, becomes more opalescent on standing, but if it is prepared under the proper conditions, reproducible values of its transmissive power can be obtained. The calculated and the experimental values of the transmissive power of the mixture methylene-blue + gelatin were the same. Hence gelatin does not adsorb the dye.

Discussion.

It has been shown that sols of proteins, such as casein, natural white of egg, purified albumin and gelatin, do not adsorb methylene-blue; the substances remain mutually uninfluenced. This result is very remarkable, because, in the precipitation of a solution of protein containing methylene-blue by means of electrolytes, the dye always comes down with the coagulum and colours it blue. Possibly in the latter case, the particles of protein may be completely dehydrated; and the activities of the hydrated and the dehydrated particles may be different.

Also aluminium hydroxide sol and methylene-blue in solution are without influence on each other. Flocculating aluminium hydroxide, however, may carry down methylene-blue. Since both substances are basic, the reason for the carrying down must be sought in some physical cause—an explanation which might be applicable to coagulating protein also. The conditions of this mechanical adsorption are of course not yet known. It must, however, be kept in mind that methylene-blue is mechanically retained by substances of many different kinds, *e.g.*, glass, filter-paper, different kinds of membranes, etc. The adsorption of methylene-blue by finely divided kaolin is also a mechanical one, as may be seen from the absorption curve. The experimental curve runs almost parallel to the calculated one and lies above it. Consequently the transmissive power observed is greater than that calculated, but here, unlike the case of silica sol or sodium silicate, no new absorption minimum results, so that there is no new specific absorption curve of the mixture to be observed. Indeed the calculated curve for the kaolin–

methylene-blue mixture has an absorption minimum, namely, that of pure methylene-blue, at $\lambda = 637\,\mu\mu$, and this does not appear in the experimental curves for very low concentrations of methylene-blue (Table III). This, however, is because the kaolin adsorbs the whole of the methylene-blue.

The absorption curve of the system silica sol + methylene-blue, on the other hand, is characteristic in that it has a new absorption minimum (quite removed from that of the methylene-blue). This and the production of a violet colour, appreciable by the naked eye, indicate chemical combination between the silica and the dye.

The same violet coloration and the same absorption minimum are obtained when a dilute solution of water-glass mixed with methylene-blue is used. The same compound is produced with its own absorption minimum at $\lambda = 590\,\mu\mu$, near which the absorption minimum of methylene-blue also is to be found.

This investigation shows that it is possible by spectrophotometric methods to determine (1) whether a dye is not adsorbed at all by colloidal adsorbents (*e.g.*, albumin, casein, gelatin,* saponin, aluminium hydroxide sol), (2) whether a mechanical adsorption takes place, *e.g.*, kaolin suspension (*lyosorption*), or (3) whether there is chemical combination between the adsorbent and the dye, *e.g.*, water-glass solution, silica sol (*chemosorption*). (See Fodor, *Koll.-chem. Beih.*, 1923, **18**, 77; "Grundlagen der Dispersoid Chemie," Dresden u. Leipzig, 1925.)

In case 1 the curves calculated from the values of a and c agree with the experimental curves.

In case 2 there is a parallel displacement upwards of the experimental curve.

In case 3 the curve has a special form with one (or perhaps several) new absorption minimum.

It is often very difficult to distinguish between chemosorption and lyosorption. In case 3, however, we believe that the appearance of a new absorption minimum indicates chemosorption. An example of the capacity of colloidal solutions to form reproducible definite stoicheiometric compounds is to be found in the case of the albumin solutions investigated by Sörensen and Höyrup (*Z. physiol. Chem.*, 1918, **103**, 104).

We have to thank Miss S. Rubinstein for help in the experimental part of the work.

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* Recent researches have shown that the phospho-protein sol from yeast-macerate is able to fix methylene-blue fairly strongly. The results will be published later.

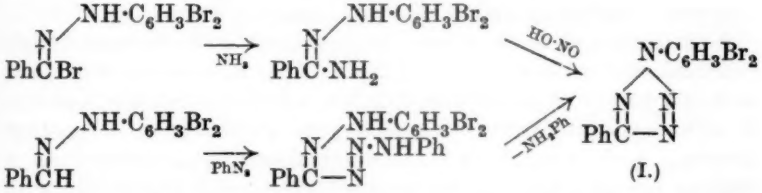
XIX.—*Substituted Dihydropentazines—A New Series of Cyclic Nitrogen Compounds.*

By FREDERICK DANIEL CHATTAWAY and GEORGE DAVID PARKES.

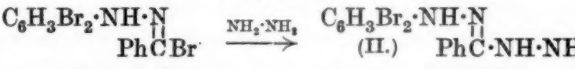
IT has recently been shown (J., 1925, **127**, 975, 1687) that when halogens react with benzaldehydephenylhydrazones substitution occurs in the hydrazine residue and in the so-called ω-position, that is, in the ·CH: group. This affords an easy method of obtaining in quantity many substituted hydrazones, in which the ω-halogen is unusually reactive.

Such ω-bromo-substituted hydrazones, for example, react with ammonia to form hydrazidines which are converted by the action of nitrous acid into tetrazoles (compare Pinner, *Ber.*, 1894, **27**, 984).

Several tetrazoles, prepared by this method, which establishes their constitution, have been shown to be identical with the compounds produced by heating the corresponding hydrazone with phenyl azide (compare Dimroth, *Ber.*, 1910, **43**, 2899). For example, benzaldehyde-2 : 4-dibromophenylhydrazone yields 1-(2 : 4-*dibromophenyl*)-4-*phenyltetrazole* by either method, thus :



These ω-halogen compounds react also with hydrazine, replacing by a hydrazino-group, the ω-halogen. For example, ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone yields *ω-hydrazinobenzaldehyde*-2 : 4-*dibromophenylhydrazone* * (II) :

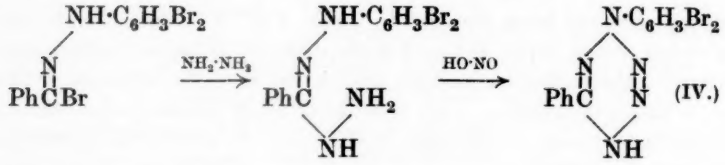


This compound behaves as a substituted hydrazine : it forms salts with halogen acids, yields an acetyl derivative when treated with acetyl chloride, and reacts with aldehydes, forming hydrazones. It also reacts with excess of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone, forming a compound having probably the constitution (III).

(III.) $C_6H_3Br_2\cdot NH\cdot N{:}CPh\cdot NH\cdot NH\cdot CPh{:}N\cdot NH\cdot C_6H_3Br_2$.

* This behaviour is in marked contrast to that of phenylhydrazine, which converts the hydrazone into a formazyl compound (compare Pechmann, *Ber.*, 1894, **27**, 322).

When treated with nitrous acid these ω-hydrazinobenzaldehyde-hydrazones are converted into dihydropentazines. Thus, for example, ω-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone yields 1-(2 : 4-*dibromophenyl*)-5-*phenyl*-1 : 4-*dihydropentazine* (IV):



(IV.)

The 5-phenyldihydropentazines are crystalline, odourless, weakly basic compounds which on being rapidly heated decompose, yielding benzonitrile.

Experimental.

Preparation of 1-(2 : 4-*Dibromophenyl*)-4-*phenyl*-1 : 2 : 3 : 5-*tetrazole* (I).—(a) *From ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone.* The hydrazone was prepared by the action of bromine upon benzaldehydephenylhydrazone and converted into the corresponding hydrazidine by boiling with an aqueous alcoholic solution of ammonia (compare Chattaway and Walker, *loc. cit.*).

A suspension of finely ground benzaldehyde-2 : 4-dibromophenylhydrazidine (5 g.) in a mixture of 20 c.c. of concentrated hydrochloric acid and 10 c.c. of water was cooled in a freezing mixture and 1 g. of solid sodium nitrite was added very gradually with constant stirring. 1-(2 : 4-*Dibromophenyl*)-4-*phenyltetrazole* separated as a slightly brown solid. It was filtered off, washed repeatedly with water, and recrystallised from boiling alcohol, in which it is moderately easily soluble and from which it separates in a felted mass of fine, white needles, m. p. 127° (Found: Br, 41·7. $C_{13}H_8N_4Br_2$ requires Br, 41·95%).

(b) *From benzaldehyde-2 : 4-dibromophenylhydrazone and phenyl azide.* A mixture of 5 g. of benzaldehyde-2 : 4-dibromophenylhydrazone, 2 g. of phenyl azide, and a solution of 0·4 g. of sodium in 8 c.c. of alcohol was heated at 100° in a sealed tube for 15 hours. The tetrazole which separated was filtered off, washed with a little alcohol, and recrystallised several times from boiling alcohol, separating as a felted mass of fine, white needles, m. p. 127°.

This and the tetrazole prepared by method (a) were identical in every respect.

1-(2 : 4-*Dibromophenyl*)-4-m-*nitrophenyl*-1 : 2 : 3 : 5-*tetrazole* (formula corresponding with I) was prepared similarly from ω-bromo-*m*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone. It separates from boiling alcohol, in which it is somewhat sparingly

soluble, in colourless needles, m. p. 215° (Found : C, 37·0; H, 1·7; N, 16·55; Br, 37·5. $C_{13}H_7O_2N_5Br_2$ requires C, 36·7; H, 1·6; N, 16·5; Br, 37·65%).

ω-Hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone (II).—A suspension of 10 g. of finely divided ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone in 50 c.c. of alcohol was added to 10 c.c. of a 50% hydrazine hydrate solution, and the mixture shaken vigorously for 15 minutes. It was then kept for 12 hours, when the whole had become a semi-solid, light brown mass. The solid was filtered off and the *ω-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone* separated from the hydrazine hydrobromide with which it was mixed, by heating it with 40—50 c.c. of alcohol and filtering hot. On cooling the warm alcoholic solution, ω-hydrazinobenzaldehyde-2 - 4-dibromophenylhydrazone separated in almost colourless needles, m. p. 123° (decomp.) (Found : Br, 41·8. $C_{13}H_{12}N_4Br_2$ requires Br, 41·7%).

This compound can be preserved unchanged for a considerable time in a sealed tube, although it darkens somewhat when exposed to light. When exposed to the air, it undergoes slow decomposition.

On adding excess of strong hydrochloric acid to a warm alcoholic solution of ω-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone the hydrochloride of the base separates on cooling as a colourless, microcrystalline powder, m. p. 188° (decomp.). The sulphate, obtained similarly, separates in minute, colourless plates which on heating decompose without melting.

ω-*Benzylidenehydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone*, $C_6H_3Br_2{\cdot}NH{\cdot}N{:}CPh{\cdot}NH{\cdot}N{:}CHPh$, is obtained as a yellow, crystalline powder on warming together in alcoholic solution equivalent quantities of benzaldehyde and ω-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone. It separates from boiling alcohol, in which it is moderately easily soluble, in small, yellow needles, m. p. 126° (Found : Br, 33·8. $C_{20}H_{16}N_4Br_2$ requires Br, 33·9%).

This compound dissolves with a yellow colour in strong alcoholic potash, and in strong sulphuric acid with a brown colour which soon changes to red.

ω-p-*Nitrobenzylidenehydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone*, $C_6H_3Br_2{\cdot}NH{\cdot}N{:}CPh{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}NO_2$, was prepared similarly from *p*-nitrobenzaldehyde. It separates from boiling alcohol in small needles which appear dark violet by transmitted light and dark green by reflected light; m. p. 194° (Found : Br, 30·8. $C_{20}H_{15}O_2N_5Br_2$ requires Br, 31·0%).

It dissolves in strong alcoholic potash with an intense blue colour, which fades almost immediately. With sulphuric acid a brown colour is produced which becomes violet on standing.

The action of a further quantity of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone upon ω-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone yields a compound, having in all probability the symmetrical constitution (III), *hydrazobenzaldehyde*-2 : 4-*dibromophenylhydrazone*.

This compound was obtained by boiling a solution of 2 g. of ω-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone and an equivalent quantity of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone in 20 c.c. of alcohol under reflux for 12 hours. A solid separated which was filtered off and recrystallised from boiling glacial acetic acid, in which it was fairly easily soluble and from which it separated in colourless needles, m. p. 237° (Found : Br, 43·2. $C_{26}H_{20}N_6Br_4$ requires Br, 43·4%).

1-(2 : 4-*Dibromophenyl*)-5-*phenyl*-1 : 4-*dihydropentazine* (IV).—Five grams of finely divided ω-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone were added to a mixture of 25 c.c. of concentrated hydrochloric acid and 25 c.c. of water, and stirred vigorously. The hydrochloride of the base separated in the course of a few minutes as a finely divided, colourless, crystalline powder. The whole was then cooled in a freezing mixture and treated with 5 g. (a considerable excess) of sodium nitrite with constant stirring. The dihydropentazine separated as a pasty, slightly brown, semi-solid mass, which was filtered off and washed repeatedly with water. It was then washed with a little light petroleum (b. p. 40—60°) and recrystallised from boiling alcohol, in which it is fairly easily soluble and from which it separates as a colourless, microcrystalline powder, m. p. 172° (decomp.) (Found : Br, 40·4; N, 17·6. $C_{13}H_9N_5Br_2$ requires Br, 40·5; N, 17·7%).

When rapidly heated alone, the compound decomposes with a puff of black smoke and formation of benzonitrile. One g. of the substance was rapidly heated in a long glass tube sealed at one end. After decomposition drops of a yellow liquid condensed on the cool parts of the tube. The tube was washed out with ether, the ethereal solution filtered, and the ether evaporated. The residual drop of yellow oily liquid, which had a smell resembling that of benzonitrile, slowly dissolved when it was boiled with aqueous sodium hydroxide, ammonia being evolved; from the cooled, acidified solution, benzoic acid was obtained which separated from boiling water in white, shining flakes, m. p. 120°. The yellow oil was therefore benzonitrile.

1-(2 : 4-Dibromophenyl)-5-phenyldihydropentazine is a colourless, crystalline solid which exhibits slightly basic properties. It is without odour and is easily soluble in the common organic solvents. It is quite stable to air and light.

The action of nitrous acid on ω-hydrazinobenzaldehyde-2 : 4-

dibromophenylhydrazone might conceivably have yielded, not the dihydropentazine, but an azide of the structure

$$C_6H_3Br_2\cdot NH\cdot N{:}CPh\cdot N<\begin{matrix}N\\ \|\\ N\end{matrix}.$$

That the compound produced has not this structure is shown by the circumstance that when heated at 100° for 60 hours in a sealed tube with acetone saturated with acetylene at 0° the whole was recovered completely unchanged. Had it possessed the azide structure it should have reacted with the acetylene, yielding 1 : 2 : 3-triazole-1-(benzaldehyde-2 : 4-dibromophenylhydrazone) (compare Dimroth, *Ber.*, 1910, **43**, 2222). Further, as mentioned above, Pinner obtained phenyltetrazole and not benzenyliminoazide by the action of nitrous acid on benzenylhydrazidine, $NH{:}CPh\cdot NH\cdot NH_2$, which is an analogous compound to the ω-hydrazino-compound from which the new ring compound was prepared. Its behaviour, therefore, is inconsistent with an azide structure, whilst it possesses the properties which would be expected in a dihydropentazine.

The formation of this compound is of considerable interest, as it contains a type of nitrogen ring apparently hitherto undescribed.

THE QUEEN'S AND KEBLE COLLEGES,
OXFORD.

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XX.—*Purification of Phosphoric Oxide.*

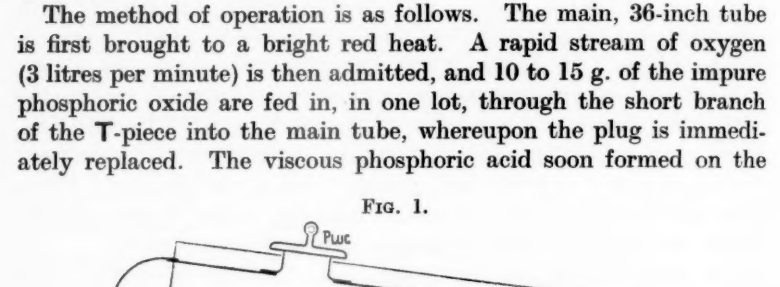
By GEORGE INGLE FINCH and REGINALD PERCY FRASER.

THE method for the purification of phosphoric oxide as devised by Finch and Peto (J., 1922, **121**, 692) has been employed in these laboratories for the last 4 years. In the light of the experience thus gained, several modifications in the original apparatus have been adopted which permit of the attaining of greater yields and increased rapidity of working. The modified form of apparatus consists of two iron tubes of 2-inch bore, the one 24 and the other 12 inches in length. These tubes are coaxially joined together by means of a 2¼-inch bore T-piece, the 1-inch long upper branch of which is machined flat and closed by the plug P, the lower surface of which is also machined. This 36-inch tube is supported in an inclined, gas-fired combustion furnace. Oxygen is led from a cylinder through glass wool into the lower end of the tube, the attachment being made by means of a length of ¼-inch iron tubing and a screwed adaptor. The cylinder oxygen employed in these laboratories is made by fractional distillation of liquid air and therefore needs no preliminary drying. The glass wool serves to retain dust. The upper and condensing end of the tube consists

of a $2\frac{1}{4}$-inch smoothly rounded, right angle bend, into the lower end of which a 2-inch length of 2-inch bore tubing is screwed. The receiver in which phosphoric oxide is condensed consists of a $1\frac{1}{2}$ litre glass-stoppered bottle, the neck of which is just sufficiently wide to admit the 2-inch bore iron tube. The right angle bend as far as the neck of the bottle is well lagged with asbestos cloth and heated by means of a large Téclu burner in order to prevent condensation in the tube itself.

The method of operation is as follows. The main, 36-inch tube is first brought to a bright red heat. A rapid stream of oxygen (3 litres per minute) is then admitted, and 10 to 15 g. of the impure phosphoric oxide are fed in, in one lot, through the short branch of the T-piece into the main tube, whereupon the plug is immediately replaced. The viscous phosphoric acid soon formed on the

FIG. 1.



machined surfaces of the plug and T-piece forms an effective seal. Rapid volatilisation of the oxide occurs, and a dense white cloud of pure crystalline phosphoric oxide is seen to condense in the receiver. A fresh charge of impure oxide is introduced as soon as the condensation due to the previous charge subsides. Glassy phosphoric acids formed in the main tube flow down towards the oxygen inlet end. They may be removed when the tube is cold by unscrewing the $\frac{1}{4}$-inch adapter and hammering the tube. The necessity for this does not arise until after several pounds of oxide have been distilled. The 24-inch section of the main tube serves to preheat the oxygen and to distil the volatile portions of the viscous oxides. The distillation section of the main tube must be kept at a bright red heat, and the right angle bend and the short piece of tubing attached to it and entering the receiver must be kept at a sufficiently high temperature to prevent condensation anywhere in the iron tube itself. At a normal rate of working,

about 500 g. of oxide can be distilled in this manner in 1 hour. The yield obtained varied from 70 to more than 80%, according to the nature of the original impure oxide and the skill of the operator. Owing to the rapid rate and the high temperature (above 800°) at which distillation occurs, a uniform crystalline product of a volume about 5 times that of the original oxide, and thus well suited for drying operations, is obtained. In order to obtain rapidly a good yield of pure product, distillation should not be commenced until the main tube is at a bright red heat with a large excess of oxygen passing through it. The receiver serves as the storage bottle, the stopper being lubricated with phosphoric oxide. The pure product obtained and stored in this manner will keep indefinitely.

The suitability of a phosphoric oxide for use in the experimental study of heterogeneous gas reactions or the attainment of a Bakerian degree of dryness depends on its vapour pressure, voluminous nature, and freedom from impurities, such as lower oxides of phosphorus and traces of organic matter. Smits and Rutgers (J., 1924, **125**, 2573) have shown that heating at temperatures above 400° yields that form of phosphoric oxide which exhibits the minimum vapour pressure. The rapid distillation carried out in the manner described above yields a crystalline product of great voluminousness. Traces of organic impurities may be detected by gently heating the moistened product in a test-tube; discoloration occurs if organic matter is present. The absence of lower oxides of phosphorus is best confirmed by the silver nitrate test described by Finch and Peto (*loc. cit.*). The mercuric chloride test also mentioned by them and advocated by Whitaker (J., 1925, **127**, 2219) has been found by us to be less sensitive than the silver nitrate test and therefore is not to be recommended.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON, S.W. [*Received, December* 18*th*, 1925.]

XXI.—*Production of Arsenic Subsulphide. Reduction of Certain Arsenic Compounds by Sodium Hyposulphite* [*Hydrosulphite*].

By WALTER FARMER and JAMES BRIERLEY FIRTH.

PRELIMINARY experiments on the reduction of certain arsenic compounds by sodium hyposulphite gave a product which was insoluble in colourless ammonium sulphide and appeared to be a subsulphide of arsenic. In the present investigation the pro-

ducts obtained by reducing various arsenic compounds in acid and in alkaline solution by sodium hyposulphite were examined.

In all the experiments the amounts of the different arsenic compounds taken were equivalent to the quantity of arsenic contained in 1 g. of pure arsenic trioxide, *i.e.*, 0·7575 g. of arsenic.

Filtration and washing of the precipitate at room temperature was a very slow process; if, however, the product was heated to boiling, the precipitate coagulated, and filtration and washing were greatly facilitated; also analysis showed that the composition of the precipitate was not affected by this treatment.

Analysis of the Product.—A solution of the precipitate was obtained by two distinct methods: (*a*) oxidation by fuming nitric acid, (*b*) oxidation by sodium peroxide in presence of hydrogen peroxide. Both methods were used for the precipitate obtained in each experiment and the two sets of results obtained showed satisfactory agreement. In each case, the arsenic was estimated as magnesium pyroarsenate (Levol, see Treadwell's "Analytical Chemistry," 1915, Vol. ii, pp. 206—208) and the sulphur as sulphate (Hentz and Weber; *op. cit.*, p. 469). To obtain a further check on the results, the arsenic remaining in the filtrate and washings was also estimated.

Series I. Reduction (a) *at* 18°, (b) *at* 0° *in Hydrochloric Acid of Definite Concentration by Sodium Hyposulphite in Various Concentrations.*—The requisite quantity of the arsenic compound was dissolved, if necessary by heating under reflux, in a mixture of 5 c.c. of concentrated hydrochloric acid and 45 c.c. of water. A solution of the requisite quantity of sodium hyposulphite in 50 c.c. of water was rapidly added, making the total volume 100 c.c. In all cases there was an immediate precipitation of a dark brown product, the quantity of which varied with the concentration of hyposulphite used.

Experiments carried out over periods ranging from 30 minutes to 12 hours showed that the duration of the experiment did not appear to affect the nature of the decomposition product, but only slightly increased the amount of the precipitate. In all subsequent experiments, therefore, the reaction was allowed to proceed for 12 hours, the reaction flask being well stoppered and the contents frequently shaken. After 12 hours, the reaction products were heated just to boiling point, and the precipitate was filtered off, thoroughly washed, dried at 100°, and weighed. In series (*b*), the solutions were cooled to 0° before mixing and the temperature of the mixed solutions was maintained at 0° for 12 hours. The results are in Table I; w = grams of hyposulphite in 100 c.c. of mixed solutions.

TABLE I.

As cmpd.	w.	(a) Reaction temp. 18°. % As ppted.	% As in ppte.	% S in ppte.	(b) Reaction temp. 0°. % As ppted.	% As in ppte.	% S in ppte.
As_2O_3	4	64·19	86·69	13·47	61·25	87·50	12·68
	6	68·74	85·63	14·51	65·39	86·38	13·78
	8	73·09	85·92	15·25	69·98	85·80	14·33
	10	79·12	84·03	16·09	75·26	84·87	15·28
As_2O_5	4	36·34	75·79	24·35	35·61	85·87	14·30
	6	37·20	74·87	25·25	36·75	85·13	15·01
	8	38·98	74·02	26·08	37·98	84·50	15·68
	10	40·05	73·41	26·75	39·78	83·81	16·31

Series II. Reduction at 18° *in Oxalic Acid Solution of Definite Concentration by Various Amounts of Sodium Hyposulphite.*—This series was carried out in order (if possible) to reduce the rate of decomposition of the sodium hyposulphite in the acid solution. The requisite quantity of the arsenic compound (= 0·7575 As) was dissolved in a solution of 4·5 g. of oxalic acid in 75 c.c. of water. The hyposulphite was dissolved in 25 c.c. of water and rapidly added to the oxalic acid solution. Other details were as before. The results are in Table II.

TABLE II.

w.	As_2O_3. % As ppted.	% As in ppte.	% S in ppte.	As_2O_5. % As ppted.	% As in ppte.	% S in ppte.
4	73·20	80·31	19·86	36·19	75·89	24·25
6	87·22	76·91	23·24	37·45	75·12	25·03
8	88·53	76·33	23·86	38·97	74·55	25·56
10	90·89	75·89	24·31	40·11	74·23	25·93

Series III. Reduction at 18° *in Hydrochloric Acid of Various Concentrations by Sodium Hyposulphite of Definite Concentration.*—In order to ascertain the effect of acid concentration, solutions of 1 g. of arsenic trioxide in 50 c.c. of hydrochloric acid of definite strength were each treated with 25 c.c. of a solution containing 10 g. of sodium hyposulphite. With increasing concentration of acid the colour changed from dark brown to very light brown. The results are in Table III*a*. This series was repeated, a quartz vessel being used. The results are in Table III*b*.

TABLE III.

As cmpd.	C.c. of conc. HCl.	% As ppted. *a.*	*b.*	% As in ppte. *a.*	*b.*	% S in ppte. *a.*	*b.*
As_2O_3	5	87·16	82·19	85·69	80·82	14·49	19·46
	10	84·26	78·65	80·96	73·78	19·25	26·47
	20	79·42	76·98	73·48	69·48	26·71	30·83
	30	74·95	71·89	62·77	56·56	37·39	43·73
	40	72·91	70·05	56·22	53·60	43·98	46·76

Series IV. Reduction in Potassium Hydroxide Solution of Definite Concentration by Sodium Hyposulphite in Various Concentrations.—Preliminary experiments showed that no dark brown precipitates were formed at room temperature, even after 3 hours. As the temperature was being raised to the boiling point of the alkaline solution in which the reduction was taking place, there was a continuous darkening of the reaction liquid followed by the formation of a dark brown precipitate, the bulk of which increased after the liquid had reached the boiling point. The escaping vapour contained a gas having a strong garlic odour. This gas was further examined. The flask containing the reaction liquid was fitted with a small reflux condenser, to the top of which a hard glass tube was attached. The reaction liquid was boiled for 30 minutes while one part of the tube was strongly heated. A white, crystalline sublimate of arsenious oxide and a metallic mirror of arsenic formed in the cooler parts of the tube. Further, the gas produced a black deposit of metallic silver in a dilute solution of silver nitrate and reacted with iodine in solution.

The subsequent experiments were carried out at the temperature of the boiling solution. A solution of the arsenic compound in 50 c.c. of 3*N*-potassium hydroxide was treated rapidly with the required amount of sodium hyposulphite dissolved in 50 c.c. of 3*N*-potassium hydroxide. The gas evolved from the boiling mixture was passed into 25 c.c. of *N*/10-iodine solution, the evolution being complete after 20 minutes. In subsequent experiments, therefore, the reaction liquid was maintained at the boiling point for 30 minutes, and was then diluted to 200 c.c. and filtered through a tared filter; the precipitate was thoroughly washed, dried, and analysed. The iodine solution was titrated with *N*/10-thiosulphate. The results are in Table IV.

TABLE IV.

As cmpd.	*w.*	% As ppted.	% As in ppte.	% S in ppte.	% As evolved.
As_2O_3	4	77·02	95·84	4·30	0·50
	6	79·75	95·68	4·49	0·50
	8	83·20	93·50	6·65	0·50
	10	86·66	89·02	11·16	0·49
As_2O_5	4	trace	—	—	0·40
	6	trace	—	—	0·40
	8	5·93	92·19	8·06	0·42
	10	8·38	90·09	10·08	0·42

Series V. Reduction at 18°, *a Neutralisation Method being used in which the Arsenic Compound dissolved in Hydrochloric Acid of Definite Volume and Concentration is reduced by Various Amounts of Sodium Hyposulphite dissolved in Potassium Hydroxide Solution of the same Volume and Normality as the Hydrochloric Acid.*—The

hyposulphite dissolved in 50 c.c. of 1·2*N*-potassium hydroxide was rapidly added to a solution of the arsenic compound in 50 c.c. of 1·2*N*-hydrochloric acid. In all cases, there was an immediate precipitation of a dark brown substance; after 12 hours, this was filtered off, washed, dried, weighed, and analysed. The results are in Table V.

TABLE V.

	Arsenic trioxide.			Trisodium arsenite.		
w.	% As ppted.	% As in ppte.	% S in ppte.	% As ppted.	% As in ppte.	% S in ppte.
4	82·75	93·18	6·96	69·79	88·09	13·12
6	88·37	93·47	6·70	76·02	88·15	13·08
8	94·81	93·62	6·57	80·05	88·21	13·02
10	99·24	93·89	6·24	87·28	88·17	13·06
	Arsenic pentoxide.			Trisodium arsenate.		
4	50·08	76·89	23·29	40·39	69·31	30·88
6	51·98	76·42	23·72	42·56	69·17	30·97
8	55·13	75·93	24·22	43·97	68·88	31·28
10	57·25	75·73	24·46	45·48	68·77	32·41

With the exception of this series (V), the results obtained with trisodium and tripotassium arsenites and arsenates were similar to those obtained with the trioxide and pentoxide respectively.

Further Examination of the Precipitates.—The precipitates obtained in the foregoing experiments were repeatedly digested with colourless ammonium sulphide until on acidifying the extract no precipitate of arsenic sulphide was obtained.

With the exception of those obtained in the experiments in alkaline solution, the precipitates contained 6, 12, 25, or 32% of sulphur. A few contained 40% or more, and some were of intermediate composition.

Products of similar composition gave similar results when digested with colourless ammonium sulphide. The following are typical examples. In the fifth experiment there was, after digestion, a very small, dark brown residue containing arsenic and sulphur.

TABLE VI.

Original As cmpd.	Exptl. condition as in series.	Comp. before digestion. % As.	% S.	Comp. after digestion. % As.	% S.	Time of digestion (days).
As_2O_3	I (*a*)	85·63	14·51	77·38	12·69	5
As_2O_5	I (*b*)	83·81	16·31	77·33	12·71	5
As_2O_3	II	80·31	19·86	77·35	12·68	7
As_2O_5	II	74·23	25·93	77·31	12·75	7
As_2O_3	III	56·22	43·98	—	—	10
As_2O_3	IV	95·84	4·30	96·11	3·92	7
As_2O_5	V	90·19	9·98	94·87	5·22	7
Na_3AsO_4	V	68·81	31·41	71·17	25·89	3
				77·41	12·81	10

The average sulphur content of the residues after extraction was 12·69% in the case of the precipitates containing initially 12·5 to 32·5% of sulphur. As As_3S requires S, 12·45%, the final product would appear to be this subsulphide, the slightly high value for sulphur being due to retention of a little arsenious sulphide, the removal of the last traces of which is very difficult. For those precipitates containing less than 12% of sulphur, the results were not so consistent; *e.g.*, for the final product from arsenic trioxide treated by the neutralisation method the mean sulphur content after extraction was 4·8%, whilst the precipitates from alkaline solutions gave final products containing 2·5 to 5·35% of sulphur.

Discussion and Conclusions.

One of the products of reduction of the arsenic compounds used is a sulphide of arsenic which contains about 12·7% of sulphur and is insoluble in colourless ammonium sulphide. It agrees in composition with the subsulphide of arsenic As_3S and appears to be identical with the substance obtained by Scott (J., 1900, **77**, 651) by treating an aqueous solution of an alkali arsenate with phosphorus trichloride and saturating the mixture with sulphur dioxide. Products containing from 2·5 to 5·35% of sulphur have also been isolated.

In moderately acid solutions tervalent arsenic compounds yield precipitates of arsenic subsulphide, As_3S, containing comparatively small quantities of arsenic trisulphide, whilst quinquevalent arsenic compounds yield precipitates which approximate in composition to the formula As_2S_3,As_3S (25·42% S). The total arsenic precipitated from the latter compounds is approximately half that from the former.

Similar results are obtained by the neutralisation method, except that the precipitates from arsenic trioxide contain 6—7%, and those from alkali arsenates 30—32%, of sulphur ($2As_2S_3,As_3S$ requires S, 29·89%).

Increase in acid concentration increases the amount of arsenic precipitated as trisulphide, and in strongly acid solutions the precipitate is mainly the trisulphide.

In alkaline solution, precipitation occurs not at room temperature but at the boiling point of the mixed solutions. In the case of arsenic trioxide the products contain 4—11% of sulphur. Arsenic pentoxide gives a comparatively small precipitate. A small amount of arsenic is volatilised at the boiling point of the mixture, mainly as trioxide associated with the hydride. The total arsenic precipitated increases, but not proportionally, with the concentration of the hyposulphite.

It would appear from the results that the subsulphide is formed by reaction between the tervalent arsenic compound and the hyposulphite, whilst the trisulphide is produced by the interaction of the arsenic compounds with thiosulphate and other thio-decomposition products of the hyposulphite. A yellow precipitate of arsenic sulphide is obtained when a solution of sodium thiosulphate containing alkali arsenite is acidified with hydrochloric acid and warmed. Hence increased concentration of hydrochloric acid increases the rate of decomposition of the hyposulphite, and the quantity of subsulphide produced is diminished and that of the trisulphide increased.

In the case of quinquevalent arsenic compounds, reduction to the tervalent compound first takes place with the production of thio-decomposition products; the arsenic is subsequently precipitated, partly as subsulphide by the hyposulphite and partly as trisulphide by the thiosulphate, etc.

At 0° (Series I*b*), the sulphur content is diminished owing to the diminution in the rate of decomposition of the hyposulphite.

In no case was the arsenic completely precipitated from solution, but in neutral solution, with 10 g. of hyposulphite for 1 g. of arsenic trioxide, 99·24% (Series V) was precipitated. The maximum precipitation of arsenic from quinquevalent compounds was 57·25%, obtained in the same series under similar conditions.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, August* 17*th*, 1925.]

XXII.—*Hydrogen Electrode Studies of the Precipitation of Basic Chromates, Borates and Carbonates.*

By HUBERT THOMAS STANLEY BRITTON.

THE work described in earlier papers (J., 1925, **127**, 2110, 2120, 2142, 2148) showed that a characteristic property of a metallic hydroxide is the hydrion concentration at which it separates from solution. The following electrometric titrations have therefore been carried out to see if the hydrogen-ion concentrations at which various basic precipitates are formed could in any way be correlated with the hydrion concentrations at which the respective hydroxides are precipitated.

I. *Basic Chromates.*

These titrations were made at 18° by the method used in the hydroxide investigations (*loc. cit.*) and chromic acid titration (Britton, J., 1924, **125**, 1572). In Table I are the particulars of the solutions and the p_H's at which precipitation took place.

TABLE I.

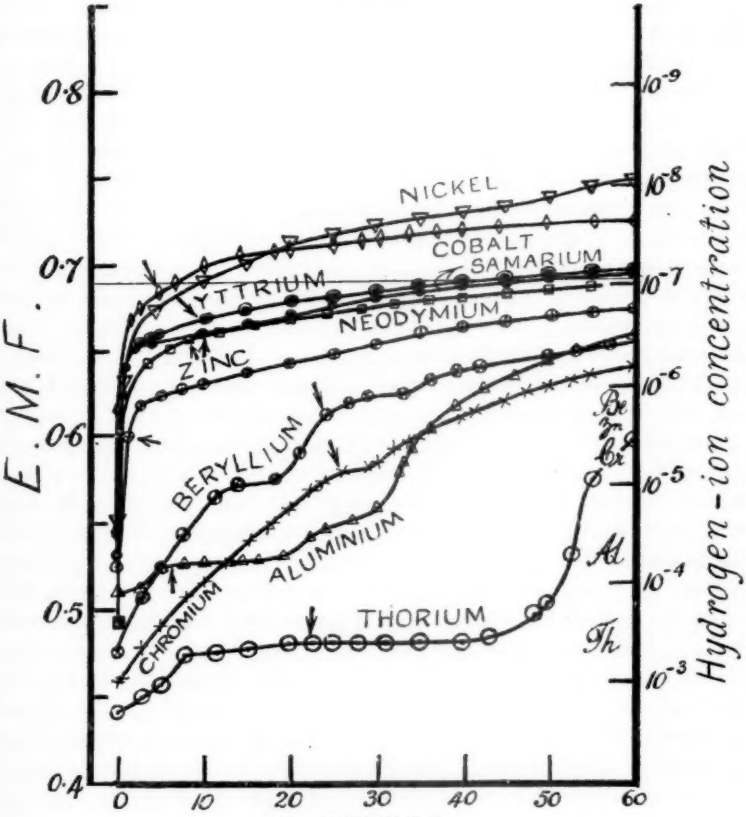
Solution (100 c.c.).	Pption of basic chromate began. *E.M.F.*	p_H.	Pption of hydroxide began. *E.M.F.*	p_H.	Pption.
0·01*M*-$ThCl_4$	0·482	3·45	0·484	3·51	Complete
0·00667*M*-$Al_2(SO_4)_3$	0·524	4·18	0·521	4·14	,,
0·01*M*-$Cr_2(SO_4)_3$,K_2SO_4	0·583	5·20	0·591	5·34	,,
0·02*M*-$BeSO_4$	0·613	5·72	0·610	5·69	,,
0·025*M*-$ZnSO_4$	0·600	5·49	0·583	5·20	
0·0132*M*-$Nd(NO_3)_3$	0·657	6·48	0·686	7·00	Partial
0·0133*M*-$SaCl_3$	0·661	6·55	0·676	6·83	,,
0·0133*M*-YCl_3	0·672	6·74	0·674	6·78	,,
0·0247*M*-$CoCl_2$	0·688	7·01	0·676	6·81	,,
0·0200*M*-$NiCl_2$	0·674	6·78	0·666	6·66	Opalescence

M/10-Potassium chromate was used in each titration except that of thorium chloride, in which case the concentration was *M*/20. The data relating to the different hydroxides were taken from the previous papers. The titration curves are given in Fig. 1, the arrows indicating the points at which precipitates first appeared.

Mechanism of the Precipitation of Basic Chromates.—Table I shows that in the majority of the titrations a precipitate did not form until the hydrogen-ion concentration of the solution had become that at which the hydroxide separates. In one or two cases the precipitate first formed was the hydroxide uncontaminated with any chromate. This was particularly the case with aluminium, the initial precipitate being aluminium hydroxide containing some unattacked sulphate. The chief factor controlling the concentration of hydrogen ions is the reaction whereby the acid, produced from the metallic salt by hydrolysis, and the potassium chromate generate hydrochromate ions. The dissociation of these ions is exceedingly small and is rendered still smaller by the increasing concentration of chromate ions from the added potassium chromate. The range of hydrogen-ion concentrations which can be produced in equilibria involving chromate and hydrochromate ions is 10^{-5} to 10^{-8}, as may be seen from the second section of the chromic acid titration curve (Britton, *loc. cit.*). For a considerable range of equilibria the hydrogen-ion concentration remains approximately 10^{-6}. The reason why potassium chromate precipitates basic chromates from salt solutions lies in the inability of the hydrochromate ions to react with the metallic bases and thus maintain them in solution, except in the few instances in which insoluble normal chromates are formed. For example, consider the reactions between freshly precipitated aluminium hydroxide and the hydrochromate ions present in potassium dichromate solutions of different concentrations. It can be shown that the p_H of *M*/10- and *M*/100-$KHCrO_4$ is 3·68 and 4·18 respectively, by assuming the salts to be completely dissociated into $K^{\cdot}$ and $HCrO_4'$, and the latter ions to

be dissociated further into an equal number of hydrogen ions and chromate ions. As aluminium hydroxide is precipitated at p_H 4·14, it follows that at the moment of formation of the precipitate the hydroxyl-ion concentration of the solution is $K_w/10^{-4\cdot14} = 10^{-10}$. In order that the aluminium hydroxide may react with the hydrochromate ions and consequently dissolve, the hydrochromate ions

FIG. 1.



must be capable of providing sufficient hydrogen ions to form water with the hydroxyl ions in the solution, *i.e.*, the product [H·][OH′] must be greater than K_w. If M/100-potassium hydrochromate solution be added to freshly precipitated aluminium hydroxide, it will set up a hydrion concentration of $10^{-4\cdot18}$, which, being less than the precipitation hydrion concentration, will be incapable of causing solution, or, in other words, [H·][OH′] will become equal to $10^{-14\cdot18}$,

a value just less than K_w, $10^{-14\cdot14}$. With M/10-$KHCrO_4$, $p_H = 3\cdot68$, the hydrogen-ion concentration will be less than that necessary for the precipitation of aluminium hydroxide and consequently there will be a tendency for the aluminium hydroxide to dissolve, the product being $10^{-13\cdot68}$, which just exceeds the ionic product of water at 18°. If thorium hydroxide, however, be used, no reaction can take place, for its precipitation p_H being 3·5, the product of the hydroxyl-ion concentration and the hydrion concentration arising from either M/10- or M/100-solution of the potassium acid chromate will be less than K_w.

The hydroxides higher in the p_H scale (*loc. cit.*, p. 2157) become increasingly reactive with the hydrochromate ions, though very little reaction takes place with those hydroxides which are precipitated from acid solutions. This is due to the fact that as soon as some hydrochromate ions have been converted into chromate ions, the hydrogen-ion concentration becomes considerably reduced and so prevents further reaction. As the hydrion concentration thereby produced is about 10^{-6}, its effect will be most marked with those hydroxides whose precipitation p_H's are above 7. The reaction between those hydroxides, which are precipitated at p_H 7 and above, and the hydrochromate radical becomes more pronounced and consequently potassium chromate causes either partial or no precipitation. Thus it is clear why potassium chromate fails to precipitate magnesium salt solutions. Magnesium hydroxide is precipitated at p_H 10·5 and is therefore able to react with the ions produced in the second stage of the ionisation of chromic acid to an extent sufficient to prevent the attainment of the p_H of precipitation. Manganous hydroxide, too, is sufficiently strong (p_H 8·4) to enter appreciably into combination with the hydrochromate radical. No precipitate is formed when potassium chromate is added to a manganous salt solution, but after some time the solution deepens in colour and eventually a brownish-black precipitate appears. This, however, is due to oxidation of the relatively large amount of manganous hydroxide present in the alkaline solution by the chromate and to some extent by the air (Gröger, *Z. anorg. Chem.*, 1905, **44**, 453).

The latter precipitation reactions may also be considered from the point of view of the alkalinity of the potassium chromate solutions. By assuming complete ionisation of the various salts involved in the hydrolysis of potassium chromate solutions, it can be shown that at 18°, $[H^+] = \sqrt{K_2 K_w / C_{K_2CrO_4}}$, K_2 of chromic acid being $4\cdot4 \times 10^{-7}$. Therefore p_H of M/10-potassium chromate is 9·75 and of the M/100-solution, 9·25. Hence the addition of potassium chromate in either of these concentrations to mag-

nesium salt solutions cannot cause precipitation, as the reactants are incapable of attaining an alkalinity corresponding to the p_H of precipitation of magnesium hydroxide. On the other hand, it appears at first sight that if a dilute manganous salt solution contained (say) $M/100$-potassium chromate, the hydrogen-ion concentration which the latter would impart, *viz.*, $10^{-9\cdot25}$, would be less than that at which manganous hydroxide is precipitated (p_H 8·4). The reaction between manganous chloride (say) and potassium chromate involves a ready reaction between manganous hydroxide and the hydrions from the first stage of ionisation of chromic acid to form some $Mn(HCrO_4)_2$ and also the more difficult reaction with the hydrions from the second stage. The result is that instead of the reaction being one of simple double decomposition, thus $K_2CrO_4 + MnCl_2 = MnCrO_4 + 2KCl$, the formation of a precipitate depends on how far the following equilibrium reaction is disturbed, $Mn(HCrO_4)_2 + Mn(OH)_2 \rightleftharpoons 2MnCrO_4 + 2H_2O$, which is governed, the oxidation effects which are peculiar to manganous and cobaltous hydroxides being excluded, by the two reactions (*a*) $HCrO_4' + OH' \rightleftharpoons CrO_4'' + H_2O$, and (*b*) $Mn^{\cdot\cdot} + 2OH' \rightleftharpoons Mn(OH)_2$. Equilibrium (*a*) is dependent on K_2 and K_w, and equilibrium (*b*) on $[Mn^{\cdot\cdot}][OH']^2$ or, more directly, the p_H of precipitation. Thus it follows that when $M/10$-potassium chromate is added to a manganous salt solution of the concentration used in these titrations, the p_H of the solution barely attains the precipitation p_H of manganous hydroxide and no precipitate is at first produced. More concentrated solutions of potassium chromate, however, effect partial but almost immediate precipitation of basic manganous chromate.

The behaviour of potassium chromate towards nickel and cobalt salt solutions is of interest. As shown in Table I, nickel hydroxide is precipitated at p_H 6·66 and cobalt hydroxide at p_H 6·81. Yet when $M/10$-potassium chromate is added to solutions of cobalt and nickel salts partial precipitation occurs in the former case and merely an opalescence is produced in the latter. The nickel and cobalt curves show that potassium chromate produces hydrion concentrations less than those at which the respective hydroxides are precipitated by alkali. The partial precipitation of cobalt is probably due to the tendency of cobalt hydroxide to oxidise. Gentle warming of the nickel solution is sufficient to cause precipitation.

The curves showing the course of precipitation of the basic chromates of neodymium and samarium have been included, for unlike the other metals except thorium, they form well-defined, difficultly soluble salts and thus the precipitation of one or the other

is determined by (*a*) the hydrogen-ion concentration and (*b*) the solubility of the normal chromate.

These hydrogen-ion relationships of the various hydroxides explain why solutions of potassium dichromate, in spite of their p_H's being greater than the precipitation p_H's of certain hydroxides, fail to cause the precipitation of basic chromates, except from zirconium salt solutions; and even in this case it is far from complete. Unless concentrated solutions be used, in which case the normal thorium chromate may be precipitated, the addition of potassium dichromate to thorium salt solutions fails to give a precipitate, although the p_H of the dichromate solution itself is greater (3·68—4·18 for solutions ranging from 0·1*M* to 0·01*M*) than the hydroxide precipitation p_H, 3·5. Potassium dichromate behaves, towards a weak base like thorium hydroxide, as a salt of a strong monobasic acid containing no reactive hydrogen atom, and on addition to a thorium salt solution merely sets up an equilibrium, $ThCl_4 + 4KHCrO_4 \rightleftharpoons Th(HCrO_4)_4 + 4KCl$, in which the thorium salt is largely hydrolysed, and thereby maintains a hydrion concentration in the solution which is much greater than that required for the precipitation of the hydroxide. An excess of potassium dichromate will have a buffering effect on the hydrolysed chromic acid, but, as the first section of the chromic acid titration curve shows, the excess would have to be considerable before the hydrogen-ion concentration could be reduced to p_H 3·5.

Detailed Study of the Precipitation Reactions.—Thorium. It was mentioned (J., 1923, **123**, 1434) that when *M*/100-thorium nitrate solution was treated with *M*/20-potassium chromate solution in stoicheiometrical amounts, precipitation was partial and the precipitate contained thoria and chromic anhydride in the molecular ratio 1 : 1·38. On substituting the chloride for the nitrate, no variation was found in the composition of the precipitate. Fig. 1 shows that 22·7 c.c. of *M*/20-potassium chromate caused the attainment of the hydroxide precipitation p_H, at which point basic thorium chromate began to be precipitated. The next 30 c.c. caused little change in p_H, but soon afterwards a rapid diminution in hydrogen-ion concentration occurred which marked the end of precipitation. On comparing the inflexion thereby produced with that in the neutralisation curve of chromic acid, it will be observed that it indicates the first half of the neutralisation of all the free chromic acid present in the solution, $KHCrO_4$ being formed. The reaction may be regarded as two simultaneous reactions: first, the gradual hydrolysis of the thorium salt thus, $ThCl_4 + 4H_2O \longrightarrow Th(OH)_4 + 4HCl$, and, secondly, $4HCl + 4K_2CrO_4 \longrightarrow 4KCl + 4KHCrO_4$.

As stated above, it would be expected that thorium hydroxide

would show a negligible tendency to react with the small concentrations of hydrions which arise from the dissociation of hydrochromate ions. Yet the thorium hydroxide which was precipitated contained appreciable amounts of chromic anhydride. Two reasons may be offered: (*a*) co-precipitation of thorium chromate, and (*b*) adsorption of chromic anhydride, through chemical forces at play between the weak base, thorium hydroxide, and the weak acid, $HCrO_4'$. The precipitates, apart from being yellow, resembled thorium hydroxide and appeared to contain no crystalline thorium chromate. Thorium chromate is much more soluble than the hydroxide, and seeing that the thorium- and chromate-ion concentrations were insufficient to produce a precipitate of the normal chromate before the hydroxide precipitation p_H was attained, it appears improbable that the basic chromate contained any normal chromate. The large chromic anhydride content of the basic precipitate was probably caused by a process akin to adsorption in which the chemical tendencies of the weak acid and the weak base played an important part.

An approximate estimate of the composition of the precipitate may be obtained from the titration curve. Precipitation was complete when 53 c.c. of *M*/20-potassium chromate had been added, *i.e.*, an amount corresponding to the mid-point of the inflexion. If thorium hydroxide alone had been precipitated, then, as shown by the previous equations, 4 mols. of potassium chromate to 1 mol. of thorium chloride would have been required, or 80 c.c. in the titration; as compared with 2 mols., or 40 c.c. of *M*/20-potassium chromate, if the normal chromate had been formed. But actually 53 c.c. were required, and therefore by alligation the basic chromate precipitate must have contained $27Th(CrO_4)_2,13Th(OH)_4$, or $ThO_2,1{\cdot}35CrO_3$. The precipitate contained 54·55% of ThO_2 and 28·47% of CrO_3, and therefore agreed with the formula $ThO_2,1{\cdot}38CrO_3,4{\cdot}57H_2O$, which is similar to that suggested by the curve.

Aluminium. Precipitation began when 5 c.c. of *M*/10-potassium chromate had been added, the p_H attained being that required for the precipitation of aluminium hydroxide. At first, the precipitate was white basic aluminium sulphate, but gradually became yellow and contained some chromate (compare Gröger, *Ber.*, 1902, **35**, 3420). The curve shows that very little change in p_H ensued until 20 c.c. of potassium chromate had been added. The main inflexion occurred and precipitation became complete when between 32 and 35 c.c. were added. The precipitate was gelatinous and contained chromate, much of which could be removed by washing.

The experiments of Gröger on the solubility of aluminium hydroxide in chromic acid solutions throw some light on the reactivity

of the acid. He found that the number of molecules of chromic anhydride required to hold 1 mol. of alumina in solution varied from 4·46 to 5·02, and therefore concluded that both aluminium chromate and dichromate were capable of existence in solution. The explanation lies in the mode of dissociation of chromic acid. The first stage of the ionisation permits of the ready solution of aluminium hydroxide, thus $Al(OH)_3 + 3H_2CrO_4 \rightleftharpoons Al(HCrO_4)_3 + 3H_2O$, which requires 6 mols. of CrO_3 to 1 mol. of Al_2O_3, but the amount of hydrions produced in the second stage of the dissociation will depend on the concentration of chromic acid used. If it be large, the great concentration of hydrochromate ions will tend to suppress the second stage of dissociation and consequently there will be proportionally fewer hydrions available for reaction than in a more dilute solution. Hence it is clear why Gröger required variable amounts of chromic acid which corresponded to somewhat less than 6 mols.

Chromium. Maus (*Pogg. Annalen*, 1827, **9**, 127) and later Storer and Eliot (*Proc. Amer. Acad. Arts Sci.*, 1862, **5**, 192) found that brown precipitates of basic chromium chromate were produced by the action of potassium chromate on solutions of chromium salts, from which the chromic acid could be removed by repeated washing. The latter investigators stated that the abstraction did not stop when the precipitate had attained any particular composition and, from an equation based on the molecular proportion of potassium chromate which they found necessary for precipitation, concluded that CrO_2, *i.e.*, Cr_2O_3,CrO_3, must have first been formed.

The titration curve shows that the factor which determined precipitation was the hydrogen-ion concentration, for when 26 c.c. of $M/10$-potassium chromate had been added and the p_H had become 5·2, as compared with 5·34 found for the hydroxide, the basic chromate began to separate. The amount of potassium chromate required was 2·6 mols. to 1 mol. of chromic sulphate, and thus happens to be about half the quantity (5 mols.) found by Storer and Eliot. As the point of precipitation is determined by the hydrion concentration, the amount of potassium chromate required appears to be a function of the concentration of the reactants. The p_H change prior to precipitation was indicated by a line which was nearly straight, comparable with the section, corresponding to the addition of the first equivalent (to 1 Cr) of sodium hydroxide, in the alkali titration curve (*loc. cit.*). The fact that 2 mols. of sodium hydroxide had to be added to 1 mol. of chromium sulphate before precipitation began was due to the peculiar property of tervalent chromium of forming "soluble basic salts," such that in a solution of the sulphate one molecule of sulphuric acid is in a state

of loose combination which may perhaps be expressed by the equilibrium $Cr_2(SO_4)_3 + 2H_2O \rightleftharpoons (OH)_2Cr_2(SO_4)_2 \ldots . H_2SO_4$, the looseness of the combination being indicated by the dotted line. This molecule of sulphuric acid, on its gradual release, reacted with two molecules of potassium chromate, thus: $H_2SO_4 + 2K_2CrO_4 = 2KHCrO_4 + K_2SO_4$, and the remaining 0·6 mol. of potassium chromate set up an equilibrium with the hydrochromate ions so formed to produce the requisite hydrion concentration for precipitation.

The precipitates formed by treating chromium sulphate solution (alum) with varying proportions of potassium chromate, corresponding to 30, 60 and 90 c.c. in the titration, were analysed. After being freed from mother-liquor by suction and a little washing by decantation, the first precipitate was green and had the composition $Cr_2O_3,0{\cdot}079CrO_3,xH_2O$, and was thus almost pure chromium hydroxide; the second was brown and contained more chromate, $Cr_2O_3,0{\cdot}574CrO_3,xH_2O$; and the third, still more, its composition being $Cr_2O_3,0{\cdot}871CrO_3,xH_2O$.

Beryllium is another of the elements that form soluble basic salts and this property appears to be reflected in the titration curve, the p_H at which precipitation began not being attained until 24 c.c. of $M/10$-potassium chromate had been added, *i.e.*, 1·2 mols. for 1 mol. of beryllium sulphate.

The alkali curve (*loc. cit.*) shows a characteristic inflexion during the reaction with the first equivalent of sodium hydroxide; precipitation occurred at p_H 5·69 (given at the top of an inflexion), when 1·04 equivalents had been added. A similar inflexion occurred in the chromate titration curve and precipitation began at p_H 5·72, indicated by a point in a similar position. The equivalent amount of potassium chromate which produced this change was 2·4 times that of the alkali and consequently the change in hydrion concentration was due to reaction between a loosely bound equivalent of acid in the beryllium sulphate molecule and potassium chromate, hydrochromate ions being formed which eventually entered into equilibrium with the added chromate ions.

Bleyer and Moorman (*Z. anorg. Chem.*, 1912, **76**, 70; see also Orlov, *ibid.*, 1913, **79**, 365) found that the interaction of potassium chromate and beryllium sulphate in solution produced very highly basic chromate precipitates, the chromate content of which seemed to increase slightly with the amount of potassium chromate added. Thus with 2 mols. of potassium chromate to one of beryllium sulphate the precipitate contained $BeO,0{\cdot}036CrO_3$, and with 4 mols. of potassium chromate, $BeO,0{\cdot}07CrO_3$, some unattacked sulphate being present in each precipitate. Bleyer and Moorman,

having found that chromic acid solutions saturated with beryllium hydroxide contained the two in equimolecular proportions, stated that beryllium chromate existed in solution. Solutions of strong acids saturated with beryllia are invariably basic, and, as shown by the titration curve of beryllium sulphate and sodium hydroxide (*loc. cit.*), the solution had to be rendered basic to an extent shown by the formula $Be(SO_4)_{0\cdot5}(OH)$ before precipitation commenced. Similarly, the proportions in Bleyer and Moorman's solutions show that they were basic to the same extent, *viz.*, $Be(HCrO_4)(OH)$, chromic acid being too weak in its second stage of dissociation to react with beryllium hydroxide to any appreciable extent.

Zinc. Table I shows that the p_H of precipitation of basic zinc chromate was 5·49 and therefore a little higher than that of the hydroxide, 5·20. The rapidity with which the p_H changed during the addition of the first c.c. of potassium chromate rendered it difficult to ascertain with any degree of precision the exact point at which the precipitate appeared. The precipitate was basic and consequently the hydrion concentration of the solution was controlled mainly by the equilibrium between the liberated hydrochromate ions and chromate ions. Gröger's analyses (*Monatsh.*, 1904, **25**, 520) showed that the precipitates obtained by treating zinc sulphate solutions with potassium chromate were indefinite and contained some sulphate, but the precipitates obtained from zinc chloride solutions were free from chloride, evidently due to the greater ease with which chlorides are hydrolysed. Varying amounts of potassium chromate were retained but were removable by washing.

An insoluble normal zinc chromate has been stated to exist by Schultze (*Z. anorg. Chem.*, 1895, **10**, 148) and Briggs (*ibid.*, 1908, **56**, 254), but the latter's data are unconvincing. It was thought that, if a difficultly soluble chromate did exist, its solubility might be too large for it to be precipitated by double decomposition through the attainment of the p_H at which the basic chromate separated, but that it might be precipitated from a chromic acid solution of zinc oxide by the gradual addition of potassium chromate so that the p_H should be kept below that necessary for the precipitation of the basic chromate (compare Britton, J., 1924, **125**, 1875). Indefinite basic chromates were always obtained; *e.g.*, one air-dried precipitate, $ZnO,0\cdot605CrO_3$, contained 55·03% ZnO and 40·90% CrO_3, and another contained 58·10% ZnO and 33·00% CrO_3, corresponding to $ZnO,0\cdot462CrO_3$.

Some criticism appears to be necessary of Gröger's conclusions (*Z. anorg. Chem.*, 1911, **70**, 135) from his study of the 25°-isotherm of the system $ZnO–CrO_3–H_2O$, in which he claims to have established

the identity of several definite basic chromates of zinc. The "rests" were considered, without experimental proof, to be the actual solid phases alone. If the molar concentrations of Gröger's liquid phases of ZnO be plotted against those of CrO_3, it will be found that all the points lie on a continuous curve, whereas had definite basic salts been formed the curve should display a number of "breaks," indicating the univariant points.

Although Gröger's conclusions can scarcely be regarded as valid, the analyses of his liquid phases are important in that they give the solubility of zinc oxide in chromic acid solutions varying in concentration from 0·006*M* to 9·7*M*, and therefore should give some idea of the reactivity of chromic acid towards zinc oxide. The number of molecules of chromic acid, H_2CrO_4, required to dissolve one molecule of zinc oxide varied continuously with increasing concentration of acid from 1·20 to 2·03, which led Gröger to conclude that the more dilute solutions contained both zinc chromate, $ZnCrO_4$, and zinc dichromate, $ZnCr_2O_7$, whilst the highly concentrated solutions contained only zinc dichromate. The fact that approximately two molecules of chromic acid were required for the most concentrated acid solutions was due to the reaction having taken place between zinc oxide and the hydrions of the first dissociation, thus: $ZnO + 2H_2CrO_4 \longrightarrow Zn(HCrO_4)_2 + H_2O$, the large concentration of hydrochromate ions having inhibited further ionisation and consequent reaction, whereas in the dilute solutions some of the hydrions from the second stage of ionisation became available for reaction, with the result that less than 2 mols. of chromic acid were required.

Cobalt and Nickel. The reactions of these two metals have already been discussed (*vide supra*).

Reference may be made to Weil's proposal (*Bull. Soc. chim.*, 1911, **9**, 20) to use potassium chromate for the separation of cobalt from nickel. Although potassium chromate does not precipitate basic nickel chromate at room temperature, the titration curve shows that the hydrion concentration produced by addition of potassium chromate to a nickel salt solution is such that the basic salt is on the point of being precipitated. A method depending on such a small difference in solubility can give but a rough separation, for there will be a great tendency for the gelatinous basic cobalt chromate to carry down much nickel.

Rare Earths.—Yttrium. Basic yttrium chromate began to be precipitated at the same p_H as its hydroxide, but precipitation was far from complete and the precipitate was highly basic. The air-dried precipitate formed by the interaction of stoicheiometrical amounts of yttrium chloride and potassium chromate (40 c.c. of

$M/10$-K_2CrO_4 in the titration) solutions contained 38·61% Y_2O_3 and 22·29% CrO_3, corresponding to the formula $Y_2O_3,1{\cdot}30CrO_3$. The filtrate from this precipitate was treated with more potassium chromate, and the new precipitate was still more basic and contained $Y_2O_3,0{\cdot}93CrO_3$.

Neodymium and Samarium. These two elements form well-defined but comparatively insoluble chromates (Britton, J., 1924, **125**, 1875); the power of these earths to unite with chromic acid in its two stages being, no doubt, due to the small solubility of the salts formed, rather than to the strength of the bases. The solubilities of praseodymium chromate and lanthanum chromate are so small that when potassium chromate is added to the respective salt solutions the conditions requisite for the precipitation of the normal chromates are obtained before the hydroxide p_H is reached. This is not so with neodymium and samarium chromates, for they are sufficiently soluble to allow the p_H at which the hydroxide is precipitated to be attained before the respective solubility products of the chromates are exceeded, and consequently basic chromate precipitates are produced. When neodymium nitrate solution was treated with potassium chromate, a flocculent precipitate was obtained which on microscopic examination was seen to contain crystalline needles similar to those of the normal chromate. The following analyses refer to precipitates so obtained: (1) Nd_2O_3, 44·13; CrO_3, 34·59%, corresponding to $Nd_2O_3,2{\cdot}64CrO_3,9{\cdot}02H_2O$, and (2) Nd_2O_3, 47·95; CrO_3, 31·81%, corresponding to $Nd_2O_3,2{\cdot}23CrO_3,7{\cdot}88H_2O$. The fact that precipitation began at p_H 6·48 instead of at 7·0, coupled with the nature of the precipitates and the relatively high CrO_3 content, indicates that the formation of these precipitates constitutes a comparatively rare example of the co-precipitation of the crystalline normal salt and an indefinite basic salt.

Samarium chromate has a greater solubility than neodymium chromate and does not appear to be precipitated with the basic chromate. As the titration curve shows, the basic chromate was precipitated at p_H 6·55, which was somewhat lower than the hydroxide p_H. It was yellow and flocculent and when dried and examined under the microscope appeared to be entirely amorphous. Its separation was partial. The air-dried precipitate from the titration contained 25·1% CrO_3 as compared with 37·84% in $Sa_2(CrO_4)_3,8H_2O$.

II. *Basic Borates.*

Electrometric titrations were carried out at 18° with $0{\cdot}05M$-borax solution and salt solutions, which were so chosen that the precipitation reactions could be studied over as wide a range of hydrogen-

ion concentration as possible. Details of the solutions used and the p_H's at which precipitates first appeared are in Table II.

TABLE II.

Solution (100 c.c. .	Pption of basic borate began.		Pption of hydroxide began.		
	E.M.F.	p_H.	*E.M.F.*	p_H.	Pption.
0·01*M*-$ZrCl_4$	0·517	4·07	0·390	1·86	Complete
0·01*M*-$ThCl_4$	0·554	4·70	0·484	3·51	,,
0·0067*M*-$Al_2(SO_4)_3$	0·521	4·14	0·521	4·14	,,
0·01*M*-$Cr_2(SO_4)_3$,K_2SO_4	0·586	5·25	0·591	5·34	,,
0·02*M*-$BeSO_4$	0·613	5·72	0·610	5·69	,,
0·02*M*-$ZnSO_4$	0·587	5·27	0·583	5·20	,,
0·02*M*-$MnCl_2$	0·792	8·82	0·770*	8·43*	Partial
			0·794	8·85	
0·02*M*-$MgSO_4$	—	—	0·885	10·49	None

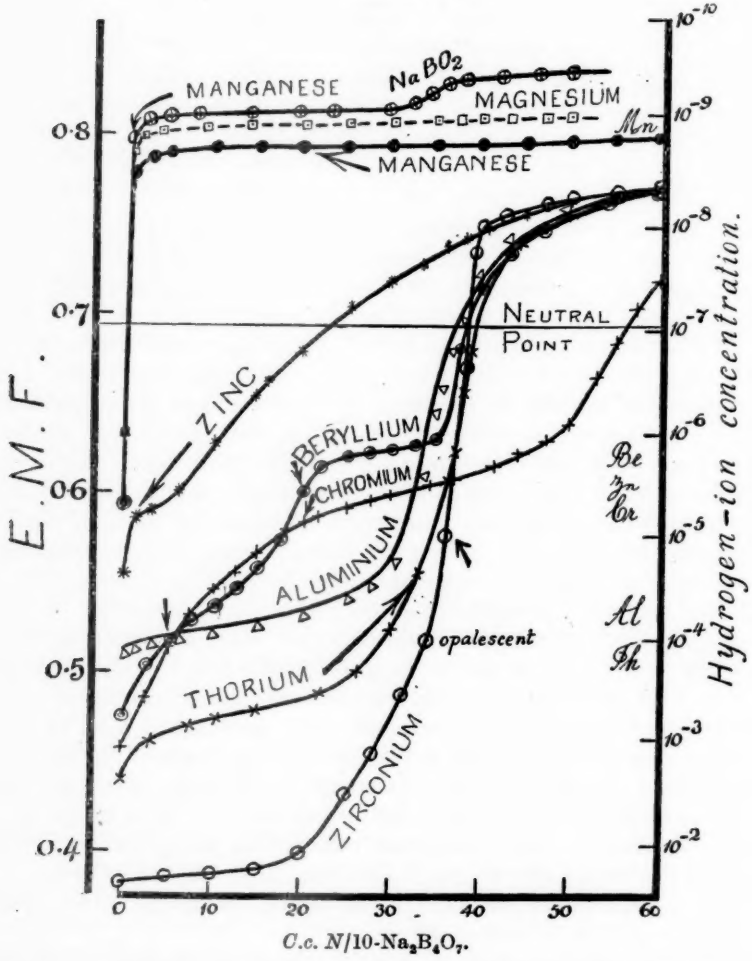
The titration curves are given in Fig. 2, the arrows showing the points at which precipitation began. The top curve in the diagram represents the titration of 100 c.c. of 0·02*M*-manganous chloride with 0·1018*M*-sodium metaborate.

Table II shows that, except in the case of zirconium and thorium, addition of borax solution did not cause precipitation to begin until the p_H at which the hydroxide is precipitated had been attained. The titration curves in Fig. 2, apart from that of zinc, are similar in shape to those representing the alkali titrations. Moreover, those curves which correspond to precipitation taking place in the acid zone show that the amounts of *N*/10-borax solution which caused the solutions to become alkaline, precipitation having become complete, were approximately the same as those required in the sodium hydroxide titrations. It appears, therefore, as far as the weaker bases are concerned, that sodium pyroborate has simply a hydrolysing action in precipitating the hydroxides, and in fact behaves as if no borate were present at all. The hydroxides which were precipitated contained some unattacked acid radical of the original salt, as may be seen from the amounts of *N*/10-borax required to render the solutions neutral, if it be assumed that the borate radical did not enter into combination. Thus in the zirconium titration, 38·5 c.c. were required as compared with the theoretical amount, 40 c.c.; thorium, 38·0 instead of 40 c.c.; aluminium, 36·0 instead of 40; chromium, 55 instead of 60; and beryllium, 37·6 instead of 40 c.c.

Provided that no insoluble normal borates are formed, it follows on theoretical grounds that boric acid, HBO_2, with its exceptionally small dissociation constant, is incapable of producing hydrogen-ion concentrations large enough to cause dissolution of any of the hydroxides which are precipitated at p_H less than 7. As far as the reactivity of boric acid is concerned, boric acid behaves as a mono-

basic acid. If 5×10^{-10} be taken as an average value of $K = [H^{\cdot}][BO_2']/[HBO_2]$, it follows that in a $M/10$-boric acid solution the hydrogen-ion concentration is $10^{-5\cdot2}$, and $10^{-5\cdot6}$ in a $M/100$-solution. The hydroxides of beryllium, zinc, chromium, aluminium,

FIG. 2.



thorium and zirconium are all precipitated at p_H less than 5·69, and consequently the hydrion concentrations of $M/10$- and $M/100$-solutions of boric acid are too small to have any solution effect on these hydroxides. Taking the case of beryllium hydroxide, which is precipitated at the highest p_H of the series under consideration,

in order that the reaction $Be(OH)_2 + 2HBO_2 \longrightarrow Be(BO_2)_2 + H_2O$ may proceed, water must be formed and therefore the product of the concentration of hydroxyl ions due to beryllium hydroxide, *viz.*, $10^{-14\cdot14}/10^{-5\cdot69} = 10^{-8\cdot45}$, and that of the hydrions from the boric acid, about $10^{-5\cdot2}$, must exceed K_w. In this case it is $10^{-13\cdot9}$, and only just exceeds K_w, and consequently beryllium hydroxide may perhaps be expected to exhibit the slightest tendency to dissolve. Any solution, however, would cause an increase in the concentration of BO_2' ions, which would depress the ionisation of boric acid and so prevent further solution. Boric acid does not dissolve either of these bases to any appreciable extent.

The hydrogen-ion concentrations of the solutions at the end of these titrations were such as would be given by borate mixtures comprising the total quantity of boric acid added and the alkali in excess of that required for the precipitations, and therefore confirm the view that no boric acid, or relatively little, was contained in the precipitates. Thus in the titrations of zinc, beryllium, aluminium, thorium and zirconium, it will be seen from Fig. 2 that the hydrion concentration when 60 c.c. of N/10-borax had been added was $10^{-8\cdot3}$ in each case. By subtracting the 40 c.c. of N/10-sodium hydroxide which were neutralised during the precipitations, it is found that the solutions contained alkali equal to 20 c.c. of N/10-sodium hydroxide and boric acid equal to 120 c.c. of N/10-HBO_2, the boric acid having been one-sixth neutralised. The p_H of a 0·2N-solution of boric acid neutralised to the same extent is, according to Sörensen, 8·29 (Prideaux, "Theory of Indicators," 1917, p. 279), and as the variation in p_H produced by the difference in concentration of the two solutions is very small, it will be seen that the agreement is sufficiently good.

Although the changes in hydrion concentration which took place in the acid zone of the titrations are almost identical with those which were obtained when the precipitant was sodium hydroxide, in the case of the weakest two bases, zirconia and thoria, the p_H's of precipitation do not compare favourably with the corresponding hydroxide p_H's. Zirconium hydroxide is generally precipitated at a p_H somewhere on the very slightly inclined part of the curve. In the precipitation of zirconium chloride solution with sodium hydroxide (J., 1925, **127**, 2124) the p_H was 1·86, but in the present titration the solution remained perfectly clear until the inflexion in the curve had been passed and the p_H had become 4·06; opalescence then began. This was when 3·4 atoms of chloride of the zirconium tetrachloride had been replaced by hydroxyl groups and, notwithstanding its highly basic nature, the solution had remained perfectly clear. With thorium chloride, the effect was similar; the

solution remained quite clear until 3·3 atoms of chloride had been replaced and the curve had begun to incline, the p_H being 4·70 instead of 3·51 obtained by using alkali. Hence it appears that the boric acid was having some restrictive influence on the size of the particles. It is probable that the tendency, although very slight, which boric acid may have to combine with thoria and zirconia exerts its greatest influence just at the point where the hydroxide or basic salt is about to pass into colloidal solution prior to precipitation. If this be the case, it seems reasonable that the boric acid, in trying to react with the nascent hydroxide, tended to keep it in solution by impeding the growth of the particles. Two experiments were made to determine whether the delayed precipitation from a thorium chloride solution whose p_H is that at which precipitation normally takes place is a matter of time: To thorium chloride solutions of the concentration used in the titration were added amounts of borax equal to 2 and 3 equivalents; in neither case did a precipitate separate during a period of several weeks.

In the chromium titration, the solution became green on addition of the borax and precipitation occurred when 21·9 c.c. of $N/10$-solution had been added, or 1·09 equivalents for each atom of chromium.

The beryllium curve again is similar to the alkali curve, and precipitation was also delayed until 21·9 c.c. (= 1·09 equivalents to 1 atom of Be) had been added.

The zinc curve shows hydrogen-ion changes which were due mainly to equilibria which must have been set up between borate ions and boric acid. The precipitation p_H was the same as that when alkali was used.

The incomplete precipitation which took place from $M/50$-manganous chloride solution will be understood when it is remembered that the p_H of $N/10$-borax itself, *viz.*, 9·11, is only slightly greater than the p_H at which manganous hydroxide is precipitated. Table II gives two p_H values for manganous hydroxide; the one marked with an asterisk is low, probably on account of oxidation of manganous hydroxide, and the other, which is approximately correct, was extrapolated from the alkali titration curve. In the borax titration the precipitate did not appear until 20 c.c. of $N/10$-borax had been added and p_H 8·82 attained. The precipitate was white and remained dispersed until 50 c.c. had been added, and, unlike the hydroxide, it did not immediately turn brown through oxidation. It readily did so when washed. (It is this protective action which is conferred on manganous hydroxide by union with some boric acid which makes the substance of use as a "drier"

in paints and varnishes.) The fact that it was precipitated at the hydroxide p_H suggests that the white precipitate was basic, and not manganous borate as was stated by Hartley and Ramage (J., 1893, **63**, 133). Their precipitates were obtained by pouring solutions of manganous sulphate into solutions of borax until no further precipitation occurred. From widely differing estimations of the manganese content only, they concluded that they had prepared a definite borate having the formula $MnH_4(BO_3)_2$ when dried at 100°, and they state that $MnH_2B_2O_5$ and $Mn(BO_2)_2$ were formed by dehydrating it still more. They also state that manganous borate was produced by the interaction of manganous sulphate and sodium metaborate. The precipitate produced by the action of *N*/10-borax on *M*/50-manganous chloride solution was both indefinite and basic and contained $MnO,1{\cdot}47HBO_2$. In the titration of *M*/50-manganous chloride with 0·1018*N*-sodium metaborate, the precipitate appeared when 1 c.c. of precipitant had been added and the p_H had become 8·77. This precipitate was, like the hydroxide, quickly oxidised and was strongly basic.

Laurent (*Comp. rend. Trav. Chim.*, 1850, **6**, 33) observed that manganous salt solutions were not precipitated with potassium hexaborate. It will be seen from the hydrogen-ion concentrations of the various borate "buffer" mixtures that the p_H of a boric acid solution, a third of which has been neutralised with alkali and which thus corresponds to Laurent's reagent, is about 8·7; this falls just below the p_H at which the hydroxide is precipitated. When, however, the borate solution is added to a manganous salt solution, some of the alkali is neutralised and the p_H falls a little further below 8·7.

According to Gmelin-Kraut ("Handbuch anorg. Chem.," 1908, iii, [2], p. 324), Berzelius found that when a magnesium salt had been added to a manganous salt solution, borax failed to give a precipitate. Neutral salts, such as sodium chloride, sodium sulphate, calcium chloride and potassium chloride, also produce this effect, but to a lesser extent; *e.g.*, a solution from which precipitation had been prevented with magnesium sulphate remained clear on standing, whereas by using either potassium chloride or any of the other salts brown precipitates appeared after 12 hours. Precipitates obtained by means of borax may be forced back into solution by the addition of these salts. Since the highest p_H that could be produced by borax solutions was far removed from the precipitation p_H of manganous hydroxide, it appeared that the behaviour of these salts in preventing precipitation of basic manganous borate lay in their power to diminish the p_H below that necessary for precipitation. For example, when 10 c.c. of a satur-

ated solution of magnesium sulphate were added to 100 c.c. of $N/10$-borax solution whose initial p_H was 9·11, the p_H fell to 8·58; with 40 c.c., p_H was 8·10; and with 50 c.c., 8·06. The effect of potassium chloride was not so marked. The addition of much potassium chloride to a $N/10$-borax solution depressed the p_H only from 9·11 to 8·82—a value, it will be noticed, corresponding to incipient precipitation.

The dotted curve shows the changes produced in hydrogen-ion concentration during the addition of $N/10$-borax solution to a $M/50$-solution of magnesium sulphate. No precipitate was obtained, for the p_H of the borax solution was below that, 10·49, requisite for the precipitation of magnesium hydroxide. Borax produces in the boiling solution a precipitate which redissolves on cooling. No precipitate was obtained with $N/10$-sodium metaborate solution, for although its p_H was 10·85, the p_H of the mixture became a little lower than the necessary value.

III. *Basic Carbonates.*

The hydrogen electrode titration method has been applied in a study of the relationships involved in the precipitation of basic carbonates. By using a plentiful supply of hydrogen electrodes which were efficient in ordinary solutions, potential differences between them and the normal calomel electrode were obtained, in these carbonate titrations, which were readily reproducible and were unaffected by any liberated carbon dioxide. Table III gives the particulars of the several titrations, and Fig. 3 shows the titration curves, the points at which precipitation began being again denoted by arrows. The sodium carbonate was decinormal in every case except the chromium titration, where it was 0·166N.

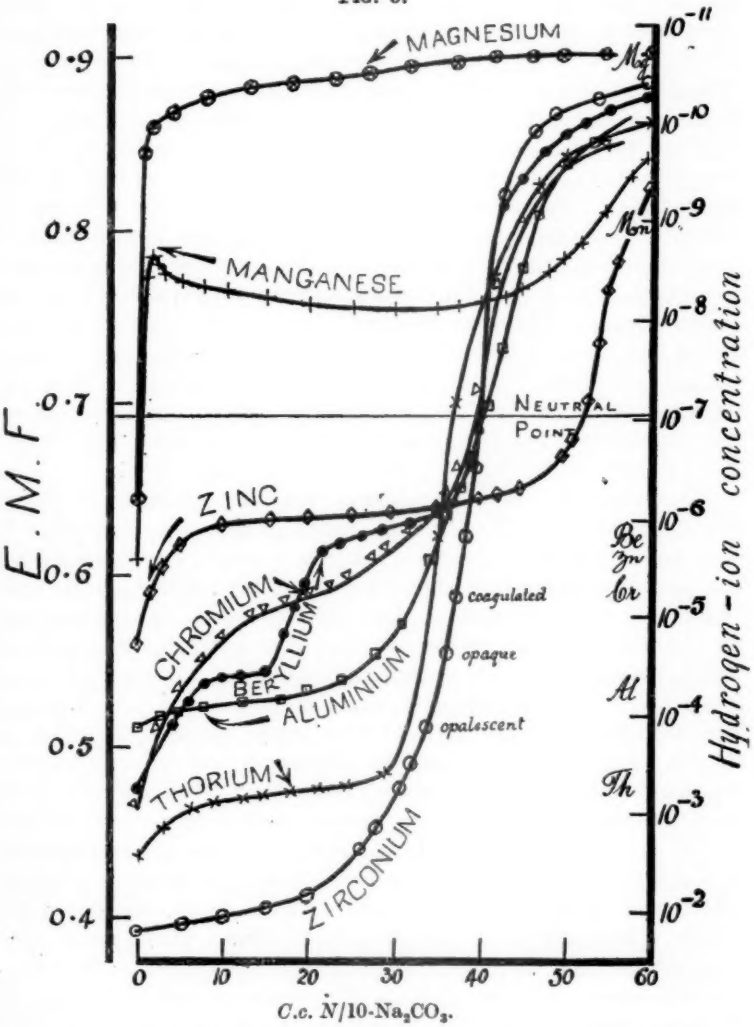
TABLE III.

	Pption of basic carbonate began.		* Pption of hydroxide began.		
Solution (100 c.c.).	*E.M.F.*	p_H.	*E.M.F.*	p_H.	Pption.
0·01M-$ZrCl_4$	0·511	3·95	0·390	1·86	Complete
0·01M-$Th(NO_3)_4$	0·476	3·35	0·484	3·51	,,
0·0067M-$Al_2(SO_4)_3$	0·523	4·16	0·521	4·14	,,
0·01M-$Cr_2(SO_4)_3$,K_2SO_4	0·587	5·27	0·591	5·34	,,
0·02M-$BeSO_4$	0·612	5·70	0·610	5·69	,,
0·02M-$ZnSO_4$	0·589	5·30	0·583	5·20	,,
0·02M-$MnCl_2$	0·784	8·68	0·794	8·85	,,
0·02M-$MgSO_4$	0·891	10·54	0·885	10·49	Turbidity

The titration curves are of the same type as those obtained in the preceding hydrolytic precipitation titrations, and in every case but zirconium, precipitation began at hydrion concentrations equal or very nearly equal to those necessary for the corresponding

hydroxides. *N*/10-Sodium carbonate, unlike the reagents used in the previous titrations, when added to the magnesium sulphate solution, produced an alkalinity corresponding, but only just so,

FIG. 3.



to the p_H at which the hydroxide is precipitated, which did not occur until 27 c.c. had been added. The precipitate formed even after 100 c.c. of sodium carbonate had been added did not amount to more than a slight turbidity.

The stoicheiometrical quantity of sodium carbonate required for simple double decomposition was equivalent to 40 c.c. of $N/10$-sodium carbonate, except in the case of chromium, where it was 36 c.c. The curves for zirconium, thorium, aluminium, beryllium and chromium show that the mother-liquors became alkaline when approximately theoretical quantities of sodium carbonate had been added. The hydrion concentrations at the end of the titrations, although differing somewhat owing to the escape of different amounts of carbon dioxide during the precipitations, were such as would be produced by mixtures of sodium bicarbonate and carbonate (compare Prideaux, "Theory of Indicators," p. 299; Auerbach and Pick, *Arb. K. Gesundheitsamt.*, 1911, **38**, 243). The changes in hydrion concentration which took place during the precipitation of the basic carbonates from solutions whose hydrogen-ion concentrations were greater than 10^{-6} were scarcely at all affected by the carbon dioxide that was liberated. The carbon dioxide set free during the precipitation of basic zinc carbonate, however, had so marked an effect on the hydrogen-ion concentration that the inflexion corresponding to the formation of sodium bicarbonate from the liberated carbon dioxide and the added sodium carbonate did not occur until 54 c.c. of the latter had been added.

The curve for manganese shows that the addition of $N/10$-sodium carbonate, after the first 2 c.c., produced a diminution in p_H, which reached a minimum, 8·2, when 30 c.c. had been added. The precipitate appeared when 1·4 c.c. had been added and p_H 8·68, *i.e.*, nearly the hydroxide p_H, had been attained. The precipitate first formed was basic, as may be seen from the curve, which shows that more than 40 c.c. of sodium carbonate had to be added before the p_H of sodium bicarbonate was attained, *viz.*, 8·7.* The precipitate, although basic, did not turn brown through oxidation by the air. It is remarkable that the increase in hydrion concentration which occurred during the titration did not cause the basic carbonate to re-dissolve. This, however, was a case of two precipitations, one of the basic carbonate due to the p_H's ruling at the beginning and at the end of the reaction, and the other of the normal carbonate, which was precipitated when the hydrion concentration of the solution was enhanced. Sodium bicarbonate when added to a manganous chloride solution, preferably saturated with carbon dioxide, causes the precipitation of manganous carbonate only, for it cannot produce a sufficiently low hydrion concentration to enable

* It may be calculated from Noyes's formula (*Z. physikal. Chem.*, 1893, **11**, 495), by taking K_1 and K_2 of carbonic acid to be 3×10^{-7} and $1{\cdot}3 \times 10^{-11}$, respectively, that the p_H of dilute solutions of sodium bicarbonate is about 8·7.

the basic carbonate to separate from solution; *e.g.*, the hydrion concentration of a manganous chloride solution was gradually reduced by the addition of a solution of sodium bicarbonate until p_H was 7·6; a white precipitate of manganous carbonate then began to form. Hence, in order to ensure the precipitation of the normal carbonate, the precipitant must be incapable of causing the p_H to be attained at which the hydroxide is precipitated.

Normal zinc carbonate has been prepared. The titration curve shows that in order to precipitate this salt uncontaminated with basic carbonate a reagent must be used which, besides causing the solubility product $[Zn^{\cdot\cdot}][CO_3'']$ to be exceeded, will maintain a hydrogen-ion concentration greater than that at which the basic carbonate would separate. Sodium bicarbonate with its p_H of 8·7 would be useless, even though the carbon dioxide which would be set free during the precipitation would tend to increase the hydrion concentration. It would be necessary to have the solution saturated with carbon dioxide under a very high pressure before any addition of sodium bicarbonate. Smith (*J. Amer. Chem. Soc.*, 1918, **40**, 883) has determined the solubility of zinc carbonate in solutions of carbon dioxide under pressures ranging from 4·12 to 40·6 atmospheres. His results may be used to calculate the hydrogen-ion concentrations of the various solutions which, being in equilibrium with zinc carbonate, were just on the point of precipitating zinc carbonate, if it be assumed, as was done by Bodländer (*Z. physikal. Chem.*, 1900, **35**, 23), that metallic bases exist in carbonic acid solutions in the form of bicarbonates. If zinc oxide exists as $Zn(HCO_3)_2$, the concentration of HCO_3' ions is equal to twice the concentration of dissolved zinc oxide, and, the extremely small concentration of hydrions arising from carbonic acid in its second stage of dissociation being neglected, it follows that $[H^{\cdot}] = [H_2CO_3]K_1/[HCO_3'] = ([CO_2] - 2[ZnO]).\ 3 \times 10^{-7}/2[ZnO]$. It was thus calculated that the p_H's of Smith's solutions varied continuously from 4·94 to 4·33. Even when the pressure of carbon dioxide is very high, the p_H at which the normal carbonate is precipitated is not very much less than that at which the hydroxide is precipitated.

Mikusch (*Z. anorg. Chem.*, 1908, **56**, 365) determined the solubility of zinc oxide in carbon dioxide solutions in equilibrium with basic zinc carbonate. By means of the above formula, it was found that the p_H's of his solutions lay between 6·05 and 6·15. These hydrion concentrations, though somewhat higher than that at which basic zinc carbonate began to separate in the present titration, *viz.*, p_H 5·3, happen to be those that obtained during the main course of the precipitation. As zinc carbonate exists in equilibrium with

hydrogen ions at a relatively high concentration, it follows that water will decompose zinc carbonate to give the less soluble basic carbonate.

The hydrogen-ion concentration which had to be attained in the magnesium titration before sodium carbonate produced a precipitate shows that, contrary to the statements of several workers, the precipitate was basic. The solubility product of magnesium carbonate, $MgCO_3,3H_2O$, at 18° is $1{\cdot}2 \times 10^{-4}$ (Johnson, *J. Amer. Chem. Soc.*, 1915, **37**, 2014), and consequently, if complete dissociation be assumed, the solubility of magnesium carbonate is $1{\cdot}1 \times 10^{-2}$ mol. per litre. The solubility of magnesium hydroxide, obtained from the solubility product, 2×10^{-11}, is $2{\cdot}7 \times 10^{-4}$ mol. per litre. Hence, to precipitate the more soluble magnesium carbonate, a precipitant must be used which will supply the necessary carbonate ions without introducing the concentration of hydroxyl ions that causes the separation of magnesium hydroxide. As magnesium hydroxide is precipitated at p_H 10·5, it is obvious that sodium bicarbonate (p_H 8·7), even although added in large excess, cannot produce the corresponding concentration of hydrogen ions, and therefore cannot precipitate basic magnesium carbonate. It can, however, supply the carbonate ions which, provided that the magnesium salt solution is sufficiently concentrated, will cause magnesium carbonate to separate. Boussingault (*Ann. Chim. Phys.*, 1825, **29**, 285) found that sodium sesquicarbonate, $Na_2CO_3,2NaHCO_3$, also could be used for this purpose. The data of Auerbach and Pick (*loc. cit.*) show that the p_H of such a mixture, decinormal with respect to carbonic acid, is approximately 9·9, which is just a little below the value required for the precipitation of the hydroxide.

No normal carbonates of chromium, beryllium, aluminium, thorium, and zirconium are known, and, as would be expected, the precipitates they form are highly basic. The shape of the beryllium titration curve appears to be peculiar to that element, and the precipitate did not appear until 22 c.c. (= 1·1 equivs. Na_2CO_3 to 1 mol. $BeSO_4$) of sodium carbonate had been added. In the chromium and thorium titrations, precipitation did not begin until 20 c.c. (1·85 equivs. to 1 Cr) and 18 c.c. (1·8 equivs.), respectively, of sodium carbonate had been added. As may be seen from Table III, the precipitation which took place from thorium chloride solution with sodium carbonate was due to the attainment of the p_H at which the hydroxide is precipitated and therefore the precipitate was basic. Chauvenet (*Compt. rend.*, 1911, **153**, 66), having found that the analysis of such a precipitate corresponded to the formula $ThO_2,CO_2,8H_2O$, stated that it was

normal thorium orthocarbonate, $ThCO_4,8H_2O$, a salt of a purely hypothetical acid. In the case of the zirconium titration the curious effect noted in the borate titration was again observed, opalescence not beginning until 3·4 equivalents of sodium carbonate had been added and the relatively high p_H of 3·95 had been attained. In the borate titration the p_H was 4·06, and 3·4 equivalents of borax were required. As mentioned above, this phenomenon is believed to be due to suppression of the growth of the basic particles owing to a slight solvent action of the liberated weak acid.

Summary.

(1) The hydrogen-ion concentrations which govern the precipitation of basic salts containing weak acid radicals—chromates, borates, and carbonates—have been investigated.

(2) These basic precipitates are formed at the same p_H as the respective hydroxides; cases occurred of delayed precipitation from zirconium and thorium chloride solutions.

(3) The precipitability of the different bases as basic salts depends on the capacity of the precipitant to produce the p_H at which the hydroxide is precipitated. In cases where this p_H is only just attained, the precipitation is partial.

(4) The conditions for the precipitation of normal salts have been discussed wherever possible.

(5) The mode of dissociation of chromic acid (J., 1924, **125**, 1572) has been shown to account for the action of alkali-metal chromates in precipitating basic salts.

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XXIII.—*Chloro-derivatives of* m-*Hydroxybenzaldehyde.*

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THE literature of this subject describes only 6-chloro- (no m. p. recorded) and 4 : 6-dichloro-3-hydroxybenzaldehydes (Friedländer and Schenck, *Ber.*, 1914, **47**, 3044), 2 : 4 : 6-trichloro-3-hydroxybenzaldehyde (Krause, *Ber.*, 1899, **32**, 123), and the conversion of

m-hydroxybenzaldehyde into aldehydotrichloroquino-dichloride by the action of chlorine in dilute acetic acid solution (Biltz and Kammann, *Ber.*, 1901, **34**, 4118).

The chlorination and the bromination (J., 1925, **127**, 876) of *m*-hydroxybenzaldehyde proceed in general on similar lines. A noteworthy difference is the production of 2-chloro-3-hydroxybenzaldehyde and but little of the 6-chloro-isomeride by direct monochlorination, bromination under similar conditions yielding 6-bromo-3-hydroxybenzaldehyde. The proportion of the 6-chloro-isomeride increases at high temperatures. The presence of water promotes trichlorination and renders regulated chlorination very difficult.

4-Chloro-3-hydroxybenzaldehyde was obtained in good yield from the corresponding 4-nitro-compound, but, as in the case of 6-bromo-3-hydroxybenzaldehyde (*loc. cit.*, p. 878), only poor yields of 6-chloro-3-hydroxybenzaldehyde were produced by a like procedure. This compound, however, was obtained in excellent yield by converting 2-chlorobenzaldehyde quantitatively into 2-chloro-5-nitrobenzaldehyde, reducing the oxime of this, diazotising the resulting 2-chloro-5-aminobenzaldoxime, and decomposing the product.

2 : 6- and 2 : 4-Dichloro-3-hydroxybenzaldehydes were obtained by direct chlorination of 2- and 4-chloro-3-hydroxybenzaldehydes, respectively, in glacial acetic acid solution, but 6-chloro-3-hydroxybenzaldehyde yielded a mixture of dichloro-compounds from which only the 2 : 6-isomeride could be isolated. In the direct dichlorination of *m*-hydroxybenzaldehyde the main product was the 2 : 6-dichloro-compound, Friedländer and Schenck's 4 : 6-dichloro-3-hydroxybenzaldehyde (*loc. cit.*) being isolated only in small quantity. The formation of the 2 : 6-dichloro-compound from both 2- and 6-chloro-3-hydroxybenzaldehyde proves the constitution assigned to it. The presence of the 4 : 6-dichloro-compound in the product of direct dichlorination of *m*-hydroxybenzaldehyde points to chlorination of the 6-monochloro-compound partially in the 4-position. Chlorination, however, takes place preferentially in position 2, and this preference is strong support for the constitution assigned to the 2 : 4-dichloro-compound obtained quantitatively from 4-chloro-3-hydroxybenzaldehyde.

The chloro-3-hydroxybenzaldehydes all have very pronounced sternutatory properties, which are most marked in the 2 : 6-, and but slightly less so in the 2 : 4 : 6-compound. For the monochloro-3-hydroxybenzaldehydes the order is 6-, 2-, and 4-. The property is comparatively feeble in the last compound, and thus is indicated its dependence on ortho-substitution. The property vanishes on methylation, but the methoxy-compounds have now acquired a hawthorn-like odour which in turn vanishes when these are oxidised

to the benzoic acids. All these compounds attack the moistened skin, producing painful blisters.

The colours produced by the action of alcoholic potash on the *p*-nitrophenylhydrazones are all claret and conform to Chattaway and Clemo's generalisation (J., 1923, **123**, 3041).

The melting points of the ethers are considerably lower than those of the hydroxy-compounds, as in the case of the bromo-compounds (*loc. cit.*, pp. 878, 879), while those of their *p*-bromophenylhydrazones exhibit noteworthy diversity.

EXPERIMENTAL.

Monochloro-3-hydroxybenzaldehydes.

2-Chloro-3-hydroxybenzaldehyde.—(a) *Preparation by direct chlorination.* Through a solution of *m*-hydroxybenzaldehyde (50 g.) in glacial acetic acid (160 g.) at 15°, chlorine was bubbled (rate about 3 g. per hour) until the increase in weight was 29 g. After 12 hours, the colourless crystals of *2-chloro-3-hydroxybenzaldehyde* were filtered off (22 g.) and recrystallised from dilute acetic acid; m. p. 139·5° (Found: Cl, 22·5. $C_7H_5O_2Cl$ requires Cl, 22·6%). The crystals become pale pink on prolonged exposure to air. On removal of 80 c.c. by distillation from the filtrate, a further crop (11 g.) was obtained, m. p. 138—140° after one recrystallisation. The solvent was then completely evaporated, and the dark residue (28 g.), m. p. 80—90°, resolved into two products by partial dissolution in hot aqueous sodium carbonate (10 g. of residue, 2 g. of Na_2CO_3, 50 c.c. of H_2O) and extraction from the cold solution with ether. The compound thus removed (3—4 g.), after two crystallisations from dilute acetic acid, had m. p. 110° and was identified as 6-chloro-3-hydroxybenzaldehyde by comparison with the synthetic product from 6-nitro-3-hydroxybenzaldehyde (see later) and with the de-alkylated product from 6-chloro-3-methoxybenzaldehyde. On acidification of the sodium carbonate solution after ether extraction, 2-chloro-3-hydroxybenzaldehyde was precipitated; this melted at 139·5° after crystallisation from dilute acetic acid.

The quantity of sodium carbonate to be used varies slightly with each chlorination experiment, the above being a good average and arrived at by trial, *viz.*, a sequence of additions, ether extractions, etc., until only 6-chloro-3-hydroxybenzaldehyde is extracted, this being much less acidic than the 2-chloro-isomeride.

Catalysts such as ferric chloride, quinoline, quinoline sulphate, and iodine have no effect on the chlorination, which proceeds equally well in carbon disulphide, chloroform, or carbon tetrachloride, apart from difficulties arising through the volatility of the solvent. Chlorine in solution is less efficient than flowing chlorine.

The above process was repeated, a stream of bromine being substituted for the stream of chlorine. 6-Bromo-3-hydroxybenzaldehyde was produced as in the regulated bromination previously described (*loc. cit.*, p. 876), but in improved yield.

(b) *Preparation from 2-nitro-3-hydroxybenzaldehyde.* The nitro-compound was reduced with sodium hyposulphite (*loc. cit.*), the mixture just acidified at 0° (Congo-paper) with hydrochloric acid, and sodium nitrite and hydrochloric acid were then added alternately with stirring until diazotisation was complete. The diazo-solution was decomposed with cuprous chloride in the usual way, and the product distilled with steam. The large distillate was concentrated to small bulk after addition of sodium carbonate, and acidified. The product extracted therefrom with ether had m. p. 139·5° after recrystallisation from dilute acetic acid and also when mixed with 2-chloro-3-hydroxybenzaldehyde prepared by method (a) (Found: Cl, 22·55. Calc., Cl, 22·6%).

Evidence for its constitution. Two g. of the presumed 2-chloro-3-hydroxybenzaldehyde obtained in (a) were treated in aqueous 20% sodium hydroxide with methyl sulphate, and the methyl ether was removed in steam and crystallised from dilute alcohol. It melted at 57°, was identical with the methyl ether of the product obtained in (b), and depressed the m. p. (52°) of 4-chloro-3-methoxybenzaldehyde. On oxidation with alkaline permanganate (*loc. cit.*, p. 880), it yielded 2-chloro-3-methoxybenzoic acid, stout, colourless rectangles, m. p. 160° (Found: Cl, 18·8. $C_8H_7O_3Cl$ requires Cl, 19·0%). 4-Chloro-3-methoxybenzoic acid forms needles, m. p. 215—216° (Found: Cl, 18·9%).

The *acetyl* derivative, m. p. 62° (Found: Cl, 18·0. $C_9H_7O_3Cl$ requires Cl, 17·9%), and the *benzoyl* derivative, m. p. 88° (Found: Cl, 13·5. $C_{14}H_9O_3Cl$ requires Cl, 13·6%), both separate from alcohol in stout, rhombic crystals. The *oxime* forms colourless needles, m. p. 149°, from diluted alcohol (Found: Cl, 20·8. $C_7H_6O_2NCl$ requires Cl, 20·7%).

The p-*nitrophenylhydrazone* crystallises in orange-red, microcrystalline needles, m. p. 244—245°, from hot alcohol (Found: N, 14·7; Cl, 12·0. $C_{13}H_{10}O_3N_3Cl$ requires N, 14·4; Cl, 12·2%).

The *semicarbazone* forms pale yellow needles, m. p. 236—237° (Found: Cl, 16·5. $C_8H_8O_2N_3Cl$ requires Cl, 16·6%).

4-*Chloro-3-hydroxybenzaldehyde.*—This compound was prepared from 4-nitro-3-hydroxybenzaldehyde by method (b) above and obtained in colourless needles, m. p. 121° (Found: Cl, 22·55. $C_7H_5O_2Cl$ requires Cl, 22·6%).

The *oxime* separates from dilute alcohol in colourless needles containing water of crystallisation. These decompose at 106—110°.

The anhydrous needles melt at 126° (Found : Cl, 20·6. $C_7H_6O_2NCl$ requires Cl, 20·7%). The p-*nitrophenylhydrazone* separates from dilute alcohol in violet-red needles, m. p. 226—227° (Found : Cl, 11·9. $C_{13}H_{10}O_3N_3Cl$ requires Cl, 12·2%), and the *semicarbazone* crystallises in pale yellow needles, m. p. 238—239° (Found : N, 20·0. $C_8H_8O_2N_3Cl$ requires N, 19·7%).

6-*Chloro*-3-*hydroxybenzaldehyde*.—(a) *Preparation from* 6-*nitro*-3-*hydroxybenzaldehyde*. This was carried out by process (b) above. The yield was very poor. The compound crystallised from dilute acetic acid in colourless needles, m. p. 111° (Found : Cl, 22·4. $C_7H_5O_2Cl$ requires Cl, 22·6%).

(b) *Preparation from* 2-*chlorobenzaldehyde*. *Nitration*. The chlorobenzaldehyde (16·5 g.) was added at 0—5° during 1 hour to a solution of sodium nitrate (11 g.) in 98% sulphuric acid (200 g.). After 30 minutes, the mixture was poured on to ice, and the solid product filtered off, washed with warm dilute sodium carbonate (yield 21 g.), and recrystallised from dilute acetic acid; m. p. 78—79° (Erdmann, *Annalen*, 1893, **272**, 153, gives m. p. 80°). (On oxidation with alkaline permanganate it gives 2-chloro-5-nitrobenzoic acid, m. p. 165°.) *Reduction*. This proceeds normally with sodium hyposulphite, but the resulting 2-chloro-5-aminobenzaldehyde gave only a trace of 6-chloro-3-hydroxybenzaldehyde on decomposition by the usual diazotisation-steam distillation process. The chloronitrobenzaldehyde was therefore converted into its oxime, m. p. 143°, and a solution of this (5·5 g.) in 20 c.c. of aqueous sodium hydroxide (20%) and 100 c.c. of water was added gradually to a mixture of crystallised ferrous sulphate (50 g.), 20% sodium hydroxide (70 c.c.), and water (200 c.c.). After being stirred for 1 hour, the mixture was warmed to 30—40°, filtered, and the filtrate just acidified; 2-*chloro*-5-*aminobenzaldoxime* was then precipitated. This crystallised from alcohol in colourless plates, m. p. 159—160°, which turned brown in the air (Found : Cl, 20·7. $C_7H_7ON_2Cl$ requires Cl, 20·8%). *Diazotisation and decomposition*. The aldoxime was redissolved by the addition of concentrated hydrochloric acid (20 c.c.), diazotised at 0° (sodium nitrite, 1·75 g.), and the solution decomposed by pouring it into boiling dilute sulphuric acid (20%). The 6-chloro-3-hydroxybenzaldehyde thus formed could be removed (very slowly) in steam, but was best extracted with ether. Yield, 3 g.

The *oxime* separates from dilute alcohol in colourless needles containing $1H_2O$ (Found : H_2O, 10·0. $C_7H_6O_2NCl,H_2O$ requires H_2O, 9·5%), and from absolute alcohol in anhydrous needles, m. p. 146—147° (Found : Cl, 20·6. $C_7H_6O_2NCl$ requires Cl, 20·7%). The p-*nitrophenylhydrazone* crystallises from dilute alcohol in red

needles, m. p. 250—251° (Found : Cl, 12·0. $C_{13}H_{10}O_3N_3Cl$ requires Cl, 12·2%).

The *semicarbazone* forms pale yellow needles, m. p. 236° (Found : N, 19·9. $C_8H_8O_2N_3Cl$ requires N, 19·7%).

Dichloro-3-hydroxybenzaldehydes.

2 : 6-*Dichloro-3-hydroxybenzaldehyde.*—(a) *Preparation by chlorination of 2-chloro-3-hydroxybenzaldehyde.* A solution of 5 g. of the aldehyde in glacial acetic acid (50 c.c.) was treated at room temperature (15°) with chlorine until the weight had increased by 2·5 g. (50 minutes). The white solid that separated crystallised from water in colourless needles, m. p. 140°. These melted at 116° when mixed with 2-chloro-3-hydroxybenzaldehyde (m. p. 139·5°) (Found : Cl, 36·8. $C_7H_4O_2Cl_2$ requires Cl, 37·1%). On concentrating the solution to 20 c.c. the bulk of the product separated. It melted at 115—118°, and at 140° after two crystallisations from water (yield 6 g.). There were no coloured by-products such as were formed during monochlorination.

(b) *Preparation from* m-*hydroxybenzaldehyde.* Through a solution of 20 g. of the aldehyde in glacial acetic acid (90 c.c.), chlorine was passed until the increase in weight was 22 g. After an interval the rate of absorption slackened, presumably when monochlorination had taken place. The product (15 g.) was collected after 12 hours and fractionally crystallised from water. The more sparingly soluble 2 : 6-dichloro-3-hydroxybenzaldehyde separated in stout, white, rhombic crystals (yield 12 g.), m. p. 140°, identical with those obtained in (a) (Found : Cl, 36·9%). From the concentrated mother-liquor 1·5 g. of a homogeneous substance separated in needles, m. p. 129°. This was identified with the 4 : 6-dichloro-3-hydroxybenzaldehyde of Friedländer and Schenck (*loc. cit.*) and was evidently formed from the 6-chloro-3-hydroxybenzaldehyde produced in the initial monochlorination (see above).

(c) *Preparation from 6-chloro-3-hydroxybenzaldehyde.* A solution of 2 g. of the aldehyde in glacial acetic acid (15 g.) was chlorinated for 18 minutes. Crystals (0·5 g.) of 2 : 6-dichloro-3-hydroxybenzaldehyde separated (m. p. 140°; mixed m. p. 140°). On evaporating the filtrate, a mixture of dichloro-compounds (1·5 g.), m. p. 120°, was obtained which has defied resolution (Found : Cl, 36·8. Calc., Cl, 37·1%). It is probably a mixture of the 2 : 6- and 4 : 6-isomerides. The *p*-nitrophenylhydrazone prepared from it melts at a lower temperature than that of either of these two compounds.

The *oxime* of 2 : 6-dichloro-3-hydroxybenzaldehyde crystallises from dilute alcohol in clusters of felted needles, m. p. 174—175° (Found : Cl, 34·2. $C_7H_5O_2NCl_2$ requires Cl, 34·5%) and the

p-*nitrophenylhydrazone* in deep orange-red needles, m. p. 205—206° (Found : Cl, 21·6. $C_{13}H_9O_3N_3Cl_2$ requires Cl, 21·8%).

2 : 4-*Dichloro*-3-*hydroxybenzaldehyde*.—The crystals obtained quantitatively by the direct chlorination of 4-chloro-3-hydroxybenzaldehyde as in (c) above melted at 136—140°, and at 141° after crystallisation from dilute acetic acid. Mixed with 2 : 6-dichloro-3-hydroxybenzaldehyde (m. p. 140°), they melted at 111° (Found : Cl, 36·9. $C_7H_4O_2Cl_2$ requires Cl, 37·1%).

The *oxime* crystallises from dilute alcohol in fine needles, m. p. 188° (Found : Cl, 34·3. $C_7H_5O_2NCl_2$ requires Cl, 34·5%), and the p-*nitrophenylhydrazone* in orange-red needles, m. p. 277—278° (decomp.) (Found : N, 13·2; Cl, 21·6. $C_{13}H_9O_3N_3Cl_2$ requires N, 12·9; Cl, 21·8%).

2 : 4 : 6-*Trichloro*-3-*hydroxybenzaldehyde*.

This is obtained normally by trichlorination in glacial acetic acid solution. The crystals separate with acetic acid of crystallisation and immediately effloresce when exposed to air. They melt at 114°, and at the same temperature after they have been crystallised from dilute acetic acid (Krause, *loc. cit.*, gives m. p. 116°).

The *sodium* salt crystallises in pure yellow needles, which are sparingly soluble in water. The *oxime* separates from dilute alcohol in needles, m. p. 174° (Krause, *loc. cit.*, gives m. p. 170°) (Found : Cl, 44·1. Calc., Cl, 44·3%).

The p-*nitrophenylhydrazone* was prepared by mixing alcoholic solutions of the components at 70° and then adding one drop of water to the cooled mixture. Crystallisation was spontaneous and the product was then almost insoluble in alcohol. It crystallises in yellow-orange, microcrystalline needles, m. p. 272—273° (decomp.) (Found : Cl, 28·9. $C_{13}H_8O_3N_3Cl_3$ requires Cl, 29·5%).

Methyl Ethers of the Chloro-3-*hydroxybenzaldehydes*.

These were prepared from the corresponding chloro-3-hydroxy- or nitro-3-methoxy-benzaldehydes by the methods used in the case of the bromo-compounds (Hodgson and Beard, *loc. cit.*, p. 878).

The following details of the methylation are reported because their adoption greatly improves the yield : a solution of 6-nitro- or 4-nitro-3-hydroxybenzaldehyde (20 g.) in water (100 c.c.) containing sodium bicarbonate (25 g.) is boiled and methyl sulphate (25 c.c.) gradually added with vigorous shaking. The mixture is heated under reflux for 15 minutes (not longer, else the yield is diminished), and the product filtered off on cooling (yield 18·5 g.).

6-*Nitro*-3-*methoxybenzoic acid*, prepared by alkaline oxidation of the aldehyde, has m. p. 255° (Rieche, *Ber.*, 1889, **22**, 2347, gives

m. p. 132—133°). It crystallises in thick, colourless prisms (Found : N, 7·0. Calc., N, 7·1%). The *silver* salt is a white, crystalline solid (Found : Ag, 35·2. Calc., Ag, 35·5%).

Nitration of 3-Methoxybenzaldehyde.—Friedländer's method (*loc. cit.*) of adding the nitric acid "*auf einmal*" proved impracticable owing to the explosive violence of the reaction.

3-Methoxybenzaldehyde (20 g.) was added drop by drop during 2 hours to a mixture of 88·1% nitric acid (94 c.c.) and water (6 c.c.) maintained below 5°. The crude product (26·5 g.) obtained on pouring the mixture on to ice was washed, dried, and dissolved in hot benzene (80 c.c.). On cooling, 2-nitro-3-methoxybenzaldehyde (12 g.) separated in crystals, m. p. 98°, and more (3 g.) was obtained on concentrating the mother-liquor. Recrystallised several times from acetic acid, it melted at 102°. The material remaining in the benzene solution, consisting mainly of 6-nitro- mixed with a little 2-nitro-3-methoxybenzaldehyde, was distilled with steam and the 6-nitro-isomeride, which is the more volatile, was thus isolated. No 4-nitro-3-methoxybenzaldehyde was detected in the mixture, for on oxidation with alkaline permanganate this yielded an acid of m. p. 250° (6-nitro-, 2-nitro-, and 4-nitro-3-methoxybenzoic acids have m. p. 255°, 251°, and 208°, respectively).

Properties of the Chloro-3-methoxybenzaldehydes.—These all crystallise in colourless needles from dilute alcohol, sublime readily, and are very volatile in steam.

2-*Chloro*-3-*methoxybenzaldehyde* has m. p. 56° (Found : Cl, 21·0. $C_8H_7O_2Cl$ requires Cl, 20·8%).

The *oxime* crystallises from dilute alcohol in stout needles, m. p. 130·5° (Found : Cl, 18·9. $C_8H_8O_2NCl$ requires Cl, 19·1%), the p-*nitrophenylhydrazone* from alcohol in old-gold needles, m. p. 226—227° (Found : N, 14·0; Cl, 11·9. $C_{14}H_{12}O_3N_3Cl$ requires N, 13·7; Cl, 11·6%), and the p-*bromophenylhydrazone* from alcohol in pale yellow plates, m. p. 155—156° (Found : N, 8·3. $C_{14}H_{12}ON_2ClBr$ requires N, 8·2%. 0·1624 G. gave 0·1592 g. of mixed silver halides. Calc., 0·1585 g.).

4-*Chloro*-3-*methoxybenzaldehyde* has m. p. 52° and acquires a beautiful silver-grey colour on keeping (Found : Cl, 20·8%).

The *oxime* crystallises in colourless feathery needles, m. p. 98—99° (Found : Cl, 18·9%), the p-*nitrophenylhydrazone* in old-gold needles, m. p. 251° (Found : N, 14·1%), and the p-*bromophenylhydrazone* in pale pink, feathery crystals, m. p. 134° (Found : N, 8·0%).

6-*Chloro*-3-*methoxybenzaldehyde* has m. p. 62° (Found : Cl, 21·2%) and on oxidation (*loc. cit.*, p. 880) yields 6-chloro-3-methoxybenzoic acid, which crystallises in needles, m. p. 170—171°, from dilute acetic acid (Found : Cl, 18·8. Calc., Cl, 19·0%). Peratoner

and Condorell (*Gazzetta*, 1898, **28**, i, 197) give 171° as the m. p. of the acid prepared from 6-chloro-3-methoxytoluene.

The *oxime* forms fine needles, m. p. 101·5° (Found : Cl, 19·0%), the p-*nitrophenylhydrazone* crystallises in old-gold needles, m. p. 229° (Found : N, 14·0%), and the p-*bromophenylhydrazone* in pale yellow plates, m. p. 100° (Found : N, 8·0%).

2 : 6-*Dichloro*-3-*methoxybenzaldehyde* has m. p. 102° (Found : Cl, 34·9. $C_8H_6O_2Cl$ requires Cl, 34·6%) and on oxidation yields 2 : 6-*dichloro*-3-*methoxybenzoic acid*, which crystallises in stout needles, m. p. 149·5°, from dilute alcohol (Found : Cl, 32·0. $C_8H_6O_3Cl_2$ requires Cl, 32·1%).

The p-*nitrophenylhydrazone* forms old-gold needles, m. p. 214—215° (Found : Cl, 20·7. $C_{14}H_{11}O_3N_3Cl_2$ requires Cl, 20·9%).

2 : 4-*Dichloro*-3-*methoxybenzaldehyde* has m. p. 82° (Found : Cl, 35·0%) and on oxidation yields 2 : 4-dichloro-3-methoxybenzoic acid, which crystallises in colourless needles, m. p. 163° (Found : Cl, 32·0%).

The p-*nitrophenylhydrazone* forms old-gold needles, m. p. 258—260° (Found : Cl, 20·7%).

2 : 4 : 6-*Trichloro*-3-*methoxybenzaldehyde* was prepared by methylating the hydroxy-compound. It is only slowly volatile in steam and crystallises from alcohol in stout needles, m. p. 76° (Found : Cl, 44·1. $C_8H_5O_2Cl_3$ requires Cl, 44·4%). By very slow oxidation with alkaline permanganate it is converted into 2 : 4 : 6-trichloro-3-methoxybenzoic acid, which crystallises in needles, m. p. 109° (Found : Cl, 41·6. Calc., Cl, 41·7%). Zincke (*Annalen*, 1891, **261**, 239) gives m. p. 90°.

The authors desire to thank the British Dyestuffs Corporation for gifts of chemicals.

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XXIV.—*The Nitration of* m-*Bromophenol.*

By HERBERT HENRY HODGSON and FRANCIS HARRY MOORE.

THE systematic study of the direct nitration of *m*-bromophenol does not appear to have been undertaken, although the following derivatives have been obtained by indirect means : 3-bromo-6-nitrophenol (Laubenheimer, *Ber.*, 1876, **9**, 1155), 3-bromo-6- and -4-nitrophenols (Auwers and Deines, *Zentr.*, 1924, II, No. 18), and 3-bromo-4 : 6-dinitrophenol (Körner, *J.*, 1876, **1**, 2317), Tijmstra (*Rec. trav. chim.*, 1902, **21**, 292) has described 3-bromo-2 : 4 : 6-trinitrophenol.

The present investigation on the direct nitration of *m*-bromophenol was carried out on similar lines to that of *m*-chlorophenol (J., 1925, **127**, 1599). 2-, 4-, and 6-Nitro-3-bromophenols, 4 : 6-, 2 : 6-, and 2 : 4-dinitro-3-bromophenols, and 2 : 4 : 6- and 2 : 5 : 6-trinitro-3-bromophenols have been prepared in excellent yield. Their properties are very similar to those of the corresponding chloro-compounds.

3-Bromo-2-nitrophenol forms a remarkably labile, colourless hydrate, m. p. 35°, which changes on keeping, particularly in dry air, to a bright yellow, anhydrous form of m. p. 65—67°; this reverts to the colourless hydrate in moist air. The sensitiveness of the compound is such as to make it an approximate indicator of atmospheric humidity. This behaviour of the substance led to a further examination of the previously reported, colourless 3-chloro-2-nitrophenol (*loc. cit.*, p. 1601), which was found to be likewise a hydrate, but much more stable in air than that of the bromo-compound. Our analyst reported on a sample which he had thoroughly dried, but made no comment on the change of colour. This we ascribed at that time to atmospheric ammonia.) The analytical datum, therefore, is for anhydrous 3-chloro-2-nitrophenol.

Since 3-bromo-5-nitrophenol has been described by Blanksma (*Rec. trav. chim.*, 1892, **21**, 254) and Heller and Kammann (*Ber.*, 1909, **42**, 2191), the anhydrous substance mentioned above must have the only remaining constitution, *viz.*, that of 3-bromo-2-nitrophenol.

The order of increasing solubility in water of the three dinitro-compounds is : 2 : 6-, 4 : 6-, and 2 : 4-. They form characteristic silver salts, that of 3-bromo-4 : 6-dinitrophenol existing in three forms (two yellow and one red); Körner's observation (*loc. cit.*) is thus confirmed and supplemented.

The orientations tentatively proposed for the dinitro-compounds follow from the modes of preparation and by analogy with the corresponding chloro-compounds (*loc. cit.*). In addition is the following evidence : (1) All three dinitro-compounds are convertible into 3-bromo-2 : 4 : 6-trinitrophenol; the two nitro-groups in each compound are therefore in the meta-position with respect to each other. (2) The constitution of 3-bromo-4 : 6-dinitrophenol is definitely settled by its preparation from 3-bromo-4- and -6-nitrophenols and from 1 : 3-dibromo-4 : 6-dinitrobenzene. (3) 3-Bromo-2 : 6- and -2 : 4-dinitrophenols not only differ in melting point and solubility and in the properties of their silver salts, but the former can be prepared from both 3-bromo-2- and -6-nitrophenols, whereas the 2 : 4-dinitro-compound is obtainable

only from a sulphonated 3-bromo-2-nitrophenol. (4) The 2 : 6- and 2 : 4-dinitro-compounds both yield 2 : 4-dinitro-*m*-phenylenediamine when heated in a sealed tube with ammonia, and each specimen of this compound gives 2 : 4-dinitroresorcinol when boiled with aqueous sodium hydroxide. The vicinal positions of the four atoms or groups in each of these two bromodinitrophenols are thus established. Also these two compounds are converted into 2 : 4-dinitroresorcinol by boiling alkalis.

After prolonged sulphonation followed by treatment with excess of nitric acid, *m*-bromophenol gives a trinitro-sulphonic acid; this on hydrolysis yields 3-bromo-2 : 5 : 6-trinitrophenol, which is volatile in steam.

EXPERIMENTAL.

Unless otherwise stated, the methods of preparation of the 3-bromonitrophenols are those of the corresponding chloro-compounds (*loc. cit.*) with appropriate modifications.

Mononitration of m-*Bromophenol.*

(a) *By Sodium Nitrate and Sulphuric Acid* (loc. cit., p. 1600).—3-*Bromo*-6-*nitrophenol* (yield 8·9 g. from 29 g. of *m*-bromophenol) is volatile in steam and crystallises from light petroleum in yellow prisms, m. p. 42°, having a characteristic odour (Auwers and Deines, m. p. 41·5—42·5°) (Found : Br, 36·7. Calc., Br, 36·7%). The methyl ether forms colourless plates, m. p. 85·5°, the benzoate crystallises in cream-coloured needles, m. p. 104°, and the sodium salt in scarlet needles. [The corresponding derivatives of 3-chloro-6-nitrophenol form colourless plates, m. p. 72°, colourless needles, m. p. 91°, and scarlet needles, respectively.]

3-*Bromo*-4-*nitrophenol* (yield 18 g.) is non-volatile in steam and crystallises from light petroleum in yellowish-white, odourless needles, m. p. 131° (Found : Br, 36·6. Calc., Br, 36·7%). It is also formed readily by oxidation of 4-nitroso-3-bromophenol (J., 1925, **127**, 2262). The methyl ether crystallises in short, colourless needles, m. p. 45°, the benzoate in cream-coloured needles, m. p. 102°, and the sodium salt in amber needles. [3-Chloro-4-nitrophenol : methyl ether, short, colourless needles, m. p. 56·5°; benzoate, colourless needles, m. p. 96°; orange sodium salt.]

(b) *By Nitric Acid in Oleum* (loc. cit., p. 1600).—On dilution of the nitration mixture and hydrolysis in a current of steam, the first distillates were oily, but from the later ones almost colourless needles separated on cooling; m. p. 35° (yield 13 g. or 60%). The product at first separated from light petroleum in bright yellow,

curly needles, m. p. 65—67°, but later crystals were admixed with the colourless product, which when separated mechanically had m. p. 33°. The yellow compound dissolves in aqueous sodium hydroxide to a red solution, from which the colourless variety is precipitated on acidification in the cold.

The yellow variety is anhydrous 3-*bromo*-2-*nitrophenol* (Found: Br, 36·6. $C_6H_4O_3NBr$ requires Br, 36·7%). It has a characteristic odour distinct from that of 3-bromo-6-nitrophenol. The *sodium* salt crystallises in red needles, the *methyl ether* from dilute alcohol in white needles, m. p. 73° (Found: Br, 34·2. $C_7H_6O_3NBr$ requires Br, 34·4%), and the *benzoate* from alcohol in white, feathery needles, m. p. 133° (Found: Br, 24·7. $C_{13}H_8O_4NBr$ requires Br, 24·8%).

The colourless variety could not be dried in sufficient quantity for analysis owing to its ready conversion into the anhydrous form and in consequence its degree of hydration has not been determined.

3-*Chloro*-2-*nitrophenol*.—The *anhydrous yellow variety*, after prolonged drying over concentrated sulphuric acid, melts at 45—47° (Found: Cl, 20·6. $C_6H_4O_3NCl$ requires Cl, 20·5%).

The hydrated white variety, crystallised from light petroleum, had m. p. 37·5—38° (Found: Cl, 18·5. $C_6H_4O_3NCl,H_2O$ requires Cl, 18·5%). On desiccation over concentrated sulphuric acid, 1·2108 g. lost 0·1128 g. after 20 hours and 0·1136 g. after 24 hours. The calculated loss for 1 mol. H_2O is 0·1138 g. (*M*, cryoscopic in phenol, 99. $C_6H_4O_3NCl$ requires *M*, 173·5; and $C_6H_4O_3NCl$, H_2O requires *M*, 96 if the water is completely abstracted by phenol).

Dinitration of m-*Bromophenol.*

The mixed acid referred to below contained 98% sulphuric acid (15 vols.), 70% nitric acid (12 vols.), and water (9 vols.).

3-*Bromo*-4 : 6-*dinitrophenol*.—(*a*) *m*-Bromophenol (4·4 g.) was added gradually to a mixture of 90·5% nitric acid (5 c.c.) and glacial acetic acid (5 c.c.), and after 12 hours the red solution was warmed for 30 minutes on the water-bath, poured into water, and steam-distilled. A little 3-bromo-6-nitrophenol passed over, followed by the main product, which solidified in colourless crystals, m. p. 90° (yield 2 g.). Recrystallised from light petroleum, this melted at 92° (Found: N, 10·7; Br, 30·4. Calc. for $C_6H_3O_5N_2Br$: N, 10·6; Br, 30·4%).

(*b*) 3-Bromo-6- and -4-nitrophenols (2 g.) were each added gradually to the mixed acid (8 c.c.) cooled in running water, the mixture was kept 2 hours, heated at 80° for 15 minutes, diluted, and steam-distilled. The product extracted from the distillate by ether crystallised from water or light petroleum in white needles,

m. p. 92°, in both cases. The liquor in the steam flask deposited in each case, on cooling, 3-bromo-2 : 4 : 6-trinitrophenol.

(*c*) 1 : 3-Dibromo-4 : 6-dinitrobenzene (3 g.) was boiled for 6 hours with aqueous sodium carbonate (3 g. in 20 c.c. of water), and the solution filtered hot and made just acid. The precipitate was crystallised from water; m. p. 92°.

The identity of the products in (*a*), (*b*), and (*c*) was established by the melting points of their mixtures.

The *silver* salt formed as a voluminous, yellow, gelatinous precipitate when a neutral solution of the ammonium salt was treated with aqueous silver nitrate. It gradually changed to a red, crystalline variety on keeping (the transition being accelerated by rubbing with a glass rod) which was but sparingly soluble in aqueous ammonia and in the presence of which conversion into a yellow, crystalline form occurred (Found : Ag, 29·0. Calc., Ag, 29·2%).

3-*Bromo*-2 : 6-*dinitrophenol*.—(*a*) This was obtained from a mixture of 1 g. of 3-bromo-2-nitrophenol and 4 c.c. of mixed acid (*loc. cit.*, p. 1602). The steam-volatile product solidified as a feathery, crystalline mass, m. p. 124°, and crystallised from light petroleum in colourless needles, m. p. 131° (Found : Br, 30·6. $C_6H_3O_5N_2Br$ requires Br, 30·4%). A non-volatile product was 3-bromo-2 : 4 : 6-trinitrophenol.

(*b*) 3-Bromo-6-nitrophenol (4 g.) was slowly added to 7 c.c. of oleum (27% SO_3) with cooling. The deep red solution was kept for 3 hours at 10°, then nitrated with 0·8 c.c. of nitric acid (90·5%) in 4 c.c. of oleum (27% SO_3), and, after 1 hour, the mixture was poured into water.

Much decomposition occurred on hydrolysis but a small quantity of 3-bromo-2 : 6-dinitrophenol was obtained, m. p. 131° (Found : Br, 30·3%).

By the same procedure 3-chloro-2 : 6-dinitrophenol was obtained from 3-chloro-6-nitrophenol.

The red, crystalline *silver* salt is fairly easily soluble in water and readily in ammonia (Found : Ag, 29·1%).

3-*Bromo*-2 : 4-*dinitrophenol* was prepared as was 3-chloro-2 : 4-dinitrophenol (*loc. cit.*, p. 1602). The steam distillate deposited 3-bromo-2 : 6-dinitrophenol (0·7 g.), which was identified by its red silver salt, m. p. 131°, and by analysis (Found : Br, 30·5%). The filtrate gave to ether 0·8 g. of a product, probably 3-bromo-2 : 4-dinitrophenol, which crystallised from water in fine, silky, cream-coloured needles, m. p. 175° (Found : Br, 30·6. $C_6H_3O_5N_2Br$ requires Br, 30·4%).

The yellow, crystalline *silver* salt was insoluble in ammonia (Found : Ag, 29%).

Attempts to prepare 3-bromo-2 : 4-dinitrophenol from 3-bromo-4-nitrophenol were unsuccessful owing to its decomposition during the sulphonation–nitration process described under (*b*) above.

Separation of a Mixture of 3-*Bromo*-2 : 6- *and* -2 : 4-*dinitrophenols.*—The mixture was converted, by the method described under 3-bromo-4 : 6-dinitrophenol above, into silver salts, which were digested with cold aqueous ammonia. The red silver salt of 3-bromo-2 : 6-dinitrophenol dissolved completely, the yellow isomeride was insoluble. The pure phenols liberated by hydrochloric acid had m. p. 131° and 175°, respectively.

Action of Ammonia on 3-*Bromo*-2 : 6- *and* -2 : 4-*dinitrophenols.*—These (1·3 g.) were separately heated in a sealed tube with concentrated ammonia (5 c.c.) to 150° during 2 hours. On cooling, the products were obtained quantitatively as brownish-yellow needles (0·9 g.) in each case, m. p. 258°. Recrystallised from water or glacial acetic acid, they melted, separately or mixed, at 258°. The substance was sparingly soluble in water, alcohol, ether, or glacial acetic acid (Found : N, 28·1 and 28·5, respectively. Calc. for $C_6H_6O_4N_4$: N, 28·3%). Barr states (*Ber.*, 1888, **21**, 1545) that 2 : 4-dinitro-*m*-phenylenediamine melts at 250° with partial decomposition. 4 : 6-Dinitro-*m*-phenylenediamine melts at about 300° (Nietzki and Schedler, *Ber.*, 1897, **30**, 1667).

The 2 : 4-dinitroresorcinol obtained from each of these products by the action of boiling aqueous sodium hydroxide melted, alone or mixed with the other, at 146° (Beilstein gives m. p. 142°) (Found : N, 14·1 and 13·9, respectively. Calc. for $C_6H_4O_6N_2$: N, 14·0%). Each product gave a red, gelatinous silver salt.

Mixtures of 3-bromo-2 : 6- and -2 : 4-dinitrophenols gave 2 : 4-dinitro-*m*-phenylenediamine when heated with ammonia as above, and 2 : 4-dinitroresorcinol on subsequent boiling with aqueous sodium hydroxide. Barr's statement (*loc. cit.*) that conversion into 2 : 4-dinitroresorcinol does not occur is therefore disproved.

Finally 3-bromo-2 : 6- and -2 : 4-dinitrophenols when separately boiled with aqueous sodium hydroxide gave the same 2 : 4-dinitroresorcinol of m. p. 146° and mixed m. p. 146°.

Trinitration of m-*Bromophenol.*

3-*Bromo*-2 : 4 : 6-*trinitrophenol*, prepared as was the corresponding chloro-compound (*loc. cit.*, p. 1603), is non-volatile in steam and crystallises from water in characteristic clusters of colourless, leaf-like forms, m. p. 149° (Tijmstra, *loc. cit.*, gives 144° for the m. p. of the compound crystallised from acetic acid) (Found : Br, 25·8. Calc., Br, 26·0%).

The same compound was also obtained by nitrating 3-bromo-

4 : 6-, -2 : 6-, and -2 : 4-dinitrophenols : 0·5 g. of each was dissolved, by gentle warming, in 98% sulphuric acid (3 c.c.), and the cooled solution treated with 70% nitric acid (1 c.c.) in 98% sulphuric acid (2 c.c.). After 3 hours, the solution was warmed on the water-bath for a few minutes and poured into water. On passage of steam, no volatile product was detected, and the solution, on cooling, deposited crystals of m. p. 149°. The yellow silver salt was insoluble in ammonia.

3-Bromo-2 : 5 : 6-trinitrophenol was prepared as was the chloro-compound (*loc. cit.*, p. 1603). It is volatile in steam and crystallises from water in fern-like clusters, m. p. 146° (Found : Br, 26·0. $C_6H_2O_7N_3Br$ requires Br, 26·0%). The yellow silver salt is soluble in water but insoluble in ammonia.

Potassium 3-bromo-2 : 5 : 6-trinitrophenol-4-sulphonate, isolated during the above preparation, gave characteristic, yellow crystals from alcohol which exploded when heated [Found : S, 6·7; Br, 17·4. Calc. for $C_6Br(OK)(NO_2)_3{\cdot}SO_3K$: S, 6·8; Br, 17·2%].

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XXV.—*Condensation of 3-Bromo- and 3-Nitro-4-dimethylaminobenzaldehyde with Ethyl Acetoacetate and Ammonia.*

By LEONARD ERIC HINKEL and WILLIAM REES MADEL.

ORTHO- and para-substituted aromatic dialkylamines do not react normally with nitrous acid (Würster and others, *Ber.*, 1879, **12**, 1796, 1816; Niementowski, *ibid.*, 1887, **20**, 1890; Koch, *ibid.*, p. 2459; Grimaux, *Compt. rend.*, 1891, **112**, 290, 727; Friedländer, *Monatsh.*, 1898, **19**, 627). We have observed that by the action of nitrous acid the aldehydo-group in *p*-dimethylaminobenzaldehyde is replaced by a nitroso-group, and that no action occurs with the corresponding 3-bromo- and 3-nitro-derivatives. It is to be expected, therefore, that the presence of a substituent in the ortho-position with respect to the dimethylamino-group will counteract any influence which this group may have on the reactivity of the aldehydo-group.

The behaviour of 3-bromo- and 3-nitro-4-dimethylaminobenzaldehyde in Hantzsch's pyridine synthesis has therefore been investigated, since it has been shown by one of us (J., 1920, **117**, 137)

that the introduction of a *p*-dimethylamino-group into benzaldehyde exerts a marked influence upon the condensation. In this case, not only is the yield of the dihydropyridine derivative considerably reduced, but the oxidation of the latter with nitrous fumes follows an unusual course, the dimethylaminophenyl group being eliminated as *p*-nitrosodimethylaniline. The dihydropyridine derivative readily yields a methiodide and a stable hydrochloride which is insoluble in water. In the condensation with 3-bromo-4-dimethylaminobenzaldehyde the effect of the introduction of the bromine atom is strikingly shown, not only in the greatly increased yield but also in the properties and the stability of the dihydrolutidine (I),

$$NH<\begin{matrix}CMe{:}C(CO_2Et)\\CMe{:}C(CO_2Et)\end{matrix}>CH\cdot C_6H_3Br\cdot NMe_2.$$

The oxidation of this compound proceeds quite normally with nitrous fumes. The dimethylamino-group, however, no longer reacts with methyl iodide even when heated under pressure, but the compound forms a hydrochloride which is very soluble in water. In this condensation the combined effects of the bromine and the dimethylamino-group cause the aldehyde to react in a manner closely resembling that of benzaldehyde.

With 3-nitro-4-dimethylaminobenzaldehyde the condensation proceeds normally. The yield of the product is not so great as in the preceding case, nevertheless it is considerably higher than that obtained from *p*-dimethylaminobenzaldehyde (*loc. cit.*), so that the influence of the nitro-group on the dimethylamino-group, although marked, is not so great as that of bromine. The stability of the dihydrolutidine derivative appears to be between those of the compounds derived from *p*-dimethylaminobenzaldehyde and its 3-bromo-derivative, since its oxidation with nitrous fumes must be more carefully regulated in order to prevent the elimination of the nitrodimethylaminophenyl group. As in the previous condensation, the dihydrolutidine derivative does not form a methiodide, but is soluble in dilute mineral acids.

The further study of the effect of substituents in benzaldehyde upon the course of Hantzsch's pyridine synthesis is in progress.

Experimental.

Ethyl 4-(m-*Bromo*-p-*dimethylaminophenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate* (I). — 3-Bromo-4-dimethylaminobenzaldehyde (1 mol.) dissolved in ethyl acetoacetate (2 mols.) was mixed with an alcoholic solution of ammonia (1 mol.). After remaining at the ordinary temperature for 1 hour, the mixture was heated for 7 hours in a closed flask. After removal of some of the alcohol the mixture solidified. The crude product crystallised from

alcohol in fine, yellowish-white needles (yield 82%), m. p. 133° (Found: Br, 17·5. $C_{21}H_{27}O_4N_2Br$ requires Br, 17·7%). The ester is very soluble in dilute hydrochloric acid and is not hydrolysed even in the boiling solution.

Ethyl 4-(m-*Bromo*-p-*dimethylaminophenyl*)-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*.—Nitrous fumes were led into a thin paste of the dihydro-ester and alcohol until a clear solution was obtained. The viscous mass obtained after removal of the alcohol slowly solidified. It crystallised from aqueous alcohol in pale yellow crystals, m. p. 91° (Found: Br, 17·7. $C_{21}H_{25}O_4N_2Br$ requires Br, 17·8%).

Hydrolysis. The ester (7 g). was boiled for several hours with 30% alcoholic potassium hydroxide (50 c.c.). No potassium salt separated (compare J., 1920, **117**, 140). The excess of potassium hydroxide was removed as carbonate, and the concentrated filtrate, after the addition of a small quantity of ether, deposited white crystals of the potassium salt.

Ethyl 4-(m-*Nitro*-p-*dimethylaminophenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate*. — 3-Nitro-4-dimethylaminobenzaldehyde (1 mol.), ethyl acetoacetate (2 mols.), and ammonia (1 mol. in alcohol) were heated together under the conditions previously described. After cooling, the solution was filtered from the crystals which had separated, and concentrated, a further crop being thus obtained. The product could be obtained in better yield by replacing ethyl acetoacetate and ammonia by ethyl β-aminocrotonate in alcoholic solution (yield 70%). The crude product crystallised from aqueous alcohol in deep yellow plates, m. p. 127° (Found: N, 10·3. $C_{21}H_{27}O_6N_3$ requires N, 10·1%).

Ethyl 4-(m-*Nitro*-p-*dimethylaminophenyl*)-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*.—The oxidation of the dihydro-ester was carried out as previously described; the nitrous fumes were, however, led in very slowly and rise in temperature prevented by external cooling with water. As soon as the dihydro-ester had dissolved, the passage of nitrous fumes was discontinued; the solution almost immediately deposited crystals, and a further crop was obtained by concentrating the mother-liquor. The base crystallised from alcohol in large, yellow crystals, m. p. 109° (Found: C, 60·6; H, 6·1; N, 10·6. $C_{21}H_{25}O_6N_3$ requires C, 60·7; H, 6·0; N, 10·1%).

We are indebted to Messrs. J. R. Geigy & Co. for a gift of the *p*-dimethylaminobenzaldehyde used in this investigation.

UNIVERSITY COLLEGE, SWANSEA. [*Received, November 19th*, 1925.]

XXVI.—*The Oxidation of Certain Sesquiterpenes with Chromyl Chloride and Chromic Acid.*

By DAVID TEMPLETON GIBSON, JOHN MONTEATH ROBERTSON, and JAMES SWORD.

THE action of chromyl chloride on the simple terpenes, as is the case with aromatic hydrocarbons, results in the formation of compounds of the formula $C_{10}H_{16},2CrO_2Cl_2$, which on treatment with water yield mixtures of oxidation products of the terpene and, as a rule, some chlorinated compounds (J., 1922, **121**, 2717; 1924, **125**, 107). Extending this work to the sesquiterpenes cadinene, β-caryophyllene, and cedrene, we now find that additive products are formed just as in the former instances, but there is a greater absorption of the reagent. The additive compound $C_{15}H_{24},2CrO_2Cl_2$ apparently is contaminated with $C_{15}H_{24},3CrO_2Cl_2$, or perhaps with $C_{15}H_{22},2CrO_2Cl$. The amount of oxidising reagent required in its formation indicates the former. These compounds are not so sensitive to atmospheric moisture as those obtained from the simple terpenes and aromatic hydrocarbons; but when they are decomposed by water they yield only a relatively small amount of tractable oxidation product.

Étard (*Ann. Chim. Phys.*, 1881, **22**, 218) states that the chromyl chloride additive product of toluene is decomposed by ether, ethyl chloride being evolved. We find, however, that ether carefully dried over sodium has no action whatever either on the toluene additive compound or on the new series of compounds we have prepared.

β-Caryophyllene forms an additive *compound* having the approximate composition $C_{15}H_{24},2\frac{1}{2}CrO_2Cl_2$. On decomposition with water, this yields a *ketone*, $C_{15}H_{24}O$ (which gave a crystalline *semicarbazone*), an *unsaturated ketone*, $C_{15}H_{20}O_2$, caryophyllene alcohol, and some chlorinated oxidation products, but no aldehyde.

From cedrene, an additive *compound* of similar composition was obtained, which on decomposition yielded a *compound*, $C_{15}H_{24}O$, which gives a *semicarbazone*, together with chlorinated products. The compound $C_{15}H_{24}O$ does not give an acid upon further oxidation with nitric acid, and is therefore probably not an aldehyde.

When the additive *compound* obtained from cadinene was decomposed, in addition to a small quantity of an acid, a 10% yield of a steam-volatile, *neutral product* was obtained which did not give a crystalline semicarbazone. Owing to the difficulty of preparing this hydrocarbon, we did not consider that the yields justified the continuation of this part of the investigation, and it seemed probable

that a direct oxidation with chromic acid might lead to more valuable results.

Wallach (*Annalen*, 1887, **238**, 87) found that, on oxidation with chromic acid, cadinene gave a mixture of lower fatty acids. With potassium dichromate and sulphuric acid mixture, we obtained products which were entirely acid. On careful oxidation with chromic anhydride, however, we obtained a *compound*, b. p. 180—196°/12 mm., the composition of which agrees with the formula $C_{15}H_{24}O_2$. No definite evidence of the presence of ketonic or hydroxyl groups could be obtained. When treated with metallic sodium, the compound polymerised. This compound closely resembles the hydroxy-ketone described by Ruzicka and Stoll (*Helv. Chim. Acta*, 1924, **7**, 94).

Experimental.

In each case described below, the additive compound was prepared by allowing the reagents to react in carbon tetrachloride solution at such dilution (10%) as allowed the course of the reaction to be carefully controlled.

Action of Chromyl Chloride on β-Caryophyllene.—β-Caryophyllene, b. p. 119°/9 mm., $n^{15°}$ 1·5030, $[\alpha]_D^{15°}$ − 5·2°, gave an additive product which had the approximate composition $C_{15}H_{24},2\frac{1}{2}CrO_2Cl_2$ and remained unaltered when different proportions of chromyl chloride were used (Found: Cr, 21·0, 20·9, 21·3. $C_{15}H_{24},2CrO_2Cl_2$ requires Cr, 20·0%. $C_{15}H_{24},3CrO_2Cl_2$ requires Cr, 23·3%). It was decomposed in the usual way. The steam-distilled oil (17 g. from 75 c.c. of caryophyllene) was fractionated at 1 mm., and a main product (10 g.), b. p. 120—140°, Cl, 5%, was collected. This fraction was practically freed from chlorine by refluxing with zinc dust in alcoholic solution for a month. The oil thus purified distilled mainly at 100—110° (A) and 110—125° (B) at 0·5 mm. (A), which was saturated, was treated (5 g.) in the usual way with semicarbazide acetate, being allowed to stand 2 months. After removal of the solvent and uncombined oil, the residue was recrystallised from methyl alcohol, and the resulting semicarbazone (1 g.), after further purification from benzene, melted at 234° (Found: C, 69·3; H, 10·0; N, 15·4. $C_{16}H_{27}ON_3$ requires C, 69·4; H, 9·8; N, 15·2%).

The uncombined oil on evaporation deposited crystals which, after washing with ligroin, melted at 92—95° and did not depress the melting point of an authentic specimen of caryophyllene alcohol.

The higher fraction (B) gave a non-crystalline semicarbazone which, after removal of solvent and uncombined oil, was distilled in steam with oxalic acid, and the regenerated oil collected. It was

unsaturated ; b. p. 118°/1 mm. (Found : C, 77·8; H, 9·4. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·9%).

Action of Chromyl Chloride on Cedrene.—Cedrene, b. p. 123—125°/8 mm., $d_4^{20°}$ 0·9361, $[\alpha]_D^{17°}$ — 55·4°, $n^{17°}$ 1·50170, gave an additive compound similar to the one described above. When it was decomposed, steam-distillation of the product gave an oil which contained chlorine (Found : Cl, 4·2%). The chlorine content was reduced to 0·5% by refluxing in alcohol with zinc dust for 8 weeks. The oil then distilled at 93°/0·15 mm., and the distillate contained no chlorine; $n^{15°}$ 1·5462 (Found : C, 81·0; H, 10·6; *M*, cryoscopic in benzene, 224, in camphor, 223. $C_{15}H_{24}O$ requires C, 81·7; H, 11·0%; *M*, 220).

The oil gave a good yield of an amorphous semicarbazone, which was dissolved in methyl alcohol to free it from the solid condensation product which semicarbazide forms with itself, purified with animal charcoal, and added to a large excess of water. This retained the last traces of the condensation product and precipitated the *semicarbazone* as a white powder (Found : C, 70·4; H, 10·0; N, 14·4. $C_{16}H_{27}ON_3$ requires C, 69·4; H, 9·8; N, 15·2%).

Action of Chromyl Chloride on Cadinene.—Cadinene, b. p. 130—134°/10 mm., $d_4^{20°}$ 0·9189, $n_D^{20°}$ 1·5097, $[\alpha]_{5461}^{18°}$ — 125°, regenerated from the dihydrochloride, m. p. 118°, gave an additive compound of similar composition to those described above. On decomposition, it yielded a small quantity of a non-crystalline acid, and a neutral product in about 10% yield, consisting of a steam-volatile oil, which was mixed with semicarbazide acetate, but even after prolonged treatment no crystalline semicarbazone could be obtained.

Chromic Acid Oxidation of Cadinene.—Chromic anhydride (70 g.) dissolved in a little water and diluted with acetic acid was slowly added with constant stirring to cadinene (50 g.) in glacial acetic acid (250 g.) during 1 hour, the temperature being kept below 50° by occasional cooling. Finally the mixture was heated on the water-bath until green, and water added. The neutral product was isolated and purified by fractional distillation at 0·5 mm. After removal of unchanged cadinene (dihydrochloride, m. p. 118°) and a small amount of acid, a light yellow oil was obtained, b. p. 180—196°/12 mm., $n_D^{6·5°}$ 1·5095 (Found : C, 76·6; H, 10·2. $C_{15}H_{24}O_2$ requires C, 76·3; H, 10·2%).

This oil was unsaturated towards bromine and alkaline permanganate. It did not give a semicarbazone, neither did it react with *p*-nitrobenzoyl chloride, or with phenylcarbimide. Addition of finely divided sodium produced polymerisation.

The acid products of the oxidation were isolated and purified.

The chief product gave the following analysis: C, 59·2; H, 8·4%. The silver salt gave Ag, 35·4%.

Cadinene (10 g.) in acetic acid (50 c.c.) was treated with potassium dichromate (20 g.) and sulphuric acid (14 c.c.) in aqueous acetic acid. The reaction was similar to that described above. After a little unchanged cadinene had been removed, there resulted only an acid product which appears to be identical with the acid described above (Found: C, 59·7; H, 8·6%. Silver salt gave Ag, 35·1%).

We desire to express our thanks to Professor G. G. Henderson for the interest which he took in this work, and to the Carnegie Trust for a grant which helped to defray the expense.

UNIVERSITY OF GLASGOW. [*Received, October 7th*, 1925.]

XXVII.—*Action of Hydrogen Fluoride on Compounds of Selenium and Tellurium. Part I. Selenium Dioxide.*

By EDMUND BRYDGES RUDHALL PRIDEAUX and JOHN O'NEIL MILLOTT.

THE action of hydrofluoric acid on selenious compounds does not appear to have been studied, except perhaps with negative results, no doubt on account of the unstable and corrosive nature of the reagents and of such compounds as they might be expected to form. Hydrofluoric acid probably does not form a definite product as it does with tellurium dioxide. A solid oxyfluoride of selenium was prepared by Moissan ("Le Fluor," p. 123) by the action of fluorine on selenium, but was not analysed. In the present research anhydrous hydrogen fluoride was used.

A remark of Ditte (*Compt. rend.*, 1876, **83**, 225) bears on the present research, *viz.*, that hydrofluoric acid is energetically absorbed by selenium dioxide; the product, however, was not examined.

Preparation of the Selenium Dioxide.—The method used was substantially that of Divers and Haga (J., 1899, **75**, 537). The selenium was dissolved in concentrated nitric acid and after several evaporations to dryness with water the product was transferred hot to a long glass tube and sublimed in a current of oxygen dried by calcium chloride and phosphoric oxide. The product was white or pink and we consider that it was dry; the test for dryness described by Prideaux and Green (*J. Physical Chem.*, 1924, **28**, 1274) was applied. The oxide, dissolved in dry alcohol, did not immediately redden litmus paper. Also a sample, heated with anhydrous copper sulphate, gave no blue colour.

Preparation of Hydrogen Fluoride—Commercial sodium hydrogen

fluoride of high quality and practically dry was finely ground and strongly heated before each distillation. This was carried out in a copper apparatus. The still, still-head, and receiver were made by Mr. E. R. Walter, B.Sc.Eng., whose skill and advice have been much appreciated. The still-head was fitted with an additional tube through which a current of dry air could be blown. The straight condenser cooled by ice-water was succeeded by a spiral condenser cooled by ice and salt. After the first runnings the liquid hydrofluoric acid was colourless and immediately gelatinised filter-paper. The receiver was then screwed on. It contained a platinum crucible, in which the acid collected, and was cooled by ice or a freezing mixture. The vapour passing on was dry, as the condensed acid would retain any traces of water. It passed over the selenium dioxide, which was usually contained in a platinum bottle supplied with platinum inlet and outlet tubes. The vapour then passed through a bubble-counter containing dry chloroform, and finally through a soda-lime tube.

The hydrogen fluoride was rapidly absorbed by the selenium dioxide, which liquefied and became warm. The liquid first formed was not analysed, but it contained quite a small proportion of hydrogen fluoride, the selenium dioxide being very soluble. As the hydrogen fluoride bubbled into the liquid it was continually absorbed. The experiment was stopped usually when the liquid contained 40 to 50% of hydrogen fluoride. This does not represent the limit of absorption from the acid vapour at a pressure somewhat below one atmosphere. In one experiment, a boat gained weight until the hydrogen fluoride was 75% of the total weight.

Properties of the Product.—The liquids formed were colourless and mobile. They fumed strongly and at the ordinary temperature the fumes consisted of hydrogen fluoride only. No volatile selenium compound was trapped in the chloroform (or alcohol) bubble-counter. The liquid does not mix with chloroform, but forms a layer below it. It rapidly attacks copper, forming a dark substance. In absence of water it slowly attacks glass. When allowed to evaporate in a desiccator with reagents which absorb water and hydrogen fluoride, it slowly dries up to a syrup. If water is present, as it was in some of our earlier experiments, crystals of selenious acid are formed, retaining less than ½% of hydrogen fluoride.

Distillation.—The product was distilled from the platinum bottle and condensed in a long platinum tube cooled with ice-water. Distillation began at about 65°, continued freely to about 85°, then fell off; little was obtained above 100° until much higher temperatures were reached. The distillate contained more selenium dioxide than can be accounted for by its vapour pressure, which

is 12·5 mm. at 70° and 40·6 mm. at 199° (Jannek and Meyer, *Z. anorg. Chem.*, 1913, **83**, 60). An analysis of the distillate is given in the first line of the table. The residue in the flask was analysed by the volumetric method. The distillate was treated with dry ether, which gave an immediate white precipitate. After washing with more ether, this contained 96 mol.% of selenium dioxide and 4 of hydrogen fluoride. In another experiment the residual liquid, from which much solid had been frozen, was distilled with sulphuric acid (the monohydrate). A yellow, fuming liquid came over at 120° to 130°. This reacted violently with water, giving a solution which contained both selenious and hydrofluoric acids, but no sulphuric acid.

The residue in the bottle after distillation (without sulphuric acid) contained slightly more than 5 mols. of hydrogen fluoride to 1 of selenium dioxide. This is the composition at which the vapour pressure of the hydrogen fluoride sinks to low values. At higher temperatures, the liquid would probably distil as a whole, with dissociation.

Separation of Solid.—Preliminary experiments showed that when the liquid was strongly cooled by alcohol–solid carbon dioxide, a white solid separated which had a composition similar to that of the liquid left after the distillation of the more volatile part. The cooling curves of this system were determined in various forms of apparatus. The arrests were variable and not well marked. This was probably due, partly to the nature of the liquid, which can be greatly supercooled, and partly to the difficulty of securing good heat transference and suitable thermal capacity in apparatus which contained so corrosive a liquid.

The freezing points were therefore determined by observation of the contents of the platinum bottle or crucible in which was placed the thermometer in a protecting tube. A portion of solution B, containing about 4·5 mols. of hydrogen fluoride to 1 of selenium dioxide, was poured into a crucible, which was cooled by direct immersion in alcohol–carbon dioxide at −70°. When crystallisation had once started, it proceeded very rapidly. The solid was allowed to melt slowly in a second crucible cooled externally. The temperature was constant at −17·5°, when about one-third was solid, and fell slowly to − 18°, when about three-quarters was solid.

Methods of Analysis.—From what is known of the strengths of hydrofluoric and selenious acids it should be possible by a volumetric method to determine approximately the amounts of each in a mixture; the greater part of the hydrofluoric acid being titrated with the first hydrion of the selenious acid with *p*-nitrophenol as indicator, and the second with an indicator of alkaline

end-point. According to the results of Willcox and Prideaux (J., 1925, **127**, 1543) the end-point in a titration of 0·05 *N*-selenious acid is at $p_H = 10{\cdot}35$; the corresponding value from Blanc's second constant is 9·70 (*loc. cit.*). Our solutions were about normal, and from the equation $2p_H = p_k + p_{kw} + \log c$, putting $\log c = 0$ and using our second constant $k_2 = [H^{\cdot}][SeO_3''']/[HSeO_3'] = 0{\cdot}87 \times 10^{-8}$, the end-point will be at $p_k = 11{\cdot}0$. The most suitable indicator available was thymolphthalein, the transition interval of which is 9·3 to 10·5. Titrations to a full blue should still be slightly below the correct end-point of the dibasic acid. This was confirmed with 10 c.c. of solutions of selenious acid.

1st end-point × 2	11·7	11·6	10·8
2nd end-point	11·6	11·5	10·65

Hydrofluoric acid is usually titrated with phenolphthalein on account of the lower degree of the second dissociation of H_2F_2. Titrations first with *p*-nitrophenol and then with phenolphthalein showed that most of the acid was neutralised at the change-point of the former indicator, the factor for converting the former into the latter titres being (on the average of several results) 1·03. The effect of the short titration with thymolphthalein on the total acid titre is negligible, and it is completely overcome by the more important error in the *p*-nitrophenol end-point of the mixed acids, which makes the volumetric estimation of selenious acid too high. The necessary corrections were determined by the following titrations of known mixtures.

	Acids separately.		Acids together.	
C.c. of alkali with *p*-nitrophenol	(*a*) 13·04	(*b*) 13·98	(*a*) 12·90	(*b*) 13·80
„ „ thymolphthalein	(*a*) 18·45	(*b*) 19·39	(*a*) 18·40	(*b*) 19·30

Thus the result of the *p*-nitrophenol titration must be multiplied by a factor, 1·01, to give the sum of the titrations of the acids separately, *i.e.*, of the hydrofluoric acid and the first hydrion of the selenious acid. This corrected titration subtracted from the total titration (with thymolphthalein) gives the amount of selenious acid. This difference, subtracted from the corrected titration with *p*-nitrophenol, gives the amount of hydrofluoric acid estimated by this indicator; and the latter, multiplied by 1·03, gives the amount of hydrofluoric acid estimated by phenolphthalein. The corrected ratios of hydrogen fluoride to selenious acid so obtained are lower than those determined gravimetrically. We have not been able to determine the reason of this discrepancy. It is possible that the hydrolysis is not quite complete, and that there is some complex formation even in aqueous solutions which diminishes the "strong acid" titration.

Selenium was determined gravimetrically by the usual method,

i.e., by precipitation with sulphur dioxide from rather concentrated hydrochloric acid. In the later experiments the modification of Lenher and Kao (*J. Amer. Chem. Soc.*, 1925, **47**, 772) was employed. The selenium was precipitated from dilute hydrochloric acid, filtered off as red selenium in the cold, washed successively with concentrated hydrochloric acid, water, alcohol, and ether, dried at 30—40°, then to constant weight at 120—130°. Under these conditions, no water or salts are included in the precipitate.

Analysis.—Attempts were made to determine the fluorine also as calcium fluoride in the presence of calcium selenite. These gave rather variable results which were low in fluorine compared with those of the two methods on which we placed most reliance. Some of the results are given in brackets under the gravimetric results in column 6 of the table, which are based on the weight of solid taken and the gravimetric selenium. Column 7 is obtained by subtracting the equivalents of selenium (gravimetric) from the total equivalents of the two acids given by the thymolphthalein titrations. The difference gives the weight of hydrogen fluoride. The sum of the selenium dioxide and the hydrogen fluoride should be equal to the weight of the solid taken. Results in which there was not a fair agreement have not been included.

Preparation *A* consisted of 19·43 g. of liquid which contained 69·3% HF. The molar ratio by increase of weight was 12·5 : 1. This was used to determine cooling curves. The first marked arrest on the cooling curve was at − 54°, the last on the heating curve, at − 29°. The liquid was then distilled up to + 85°. The analysis of the distillate is given in the table. The residue, by titration only, contained hydrogen fluoride and selenium dioxide in the ratio 4·9. Two samples of solid separated from the mother-liquor and titrated without weighing gave ratios of 4·9 and 4·93.

Preparation *B* weighed 21·91 g. and the molar ratio by increase of weight was 4·425. The initial arrest on the cooling curve was at − 22·5°. The solid B_1 was frozen out and analysed. The residue in the bottle, which had now been reduced to 14·8 g., was poured into a crucible and the freezing point determined as described above. The remaining samples of *B* were then taken and analysed.

The filtration of B_1 was done in the usual way, except that the crucible was surrounded by a glass tube, containing lumps of solid carbon dioxide and closed at the top by a stopper in which was a calcium chloride tube to dry the incoming air. The platinum Gooch crucible contained dried asbestos fibre, above which was a false bottom of platinum foil perforated with needle holes. The liquid which had run through the asbestos was rejected. The solid was removed quickly and weighed in a closed crucible. Sample

B_2 was pressed on the Gooch crucible with the false bottom but without the asbestos. It was kept cold inside another crucible in the freezing mixture. Sample B_3 was washed with dry cold chloroform by decantation and dried with filter-paper until strong fuming began. Preparation C, 17·54 g., had a molar ratio of 4·62 to 1. The fractions C_1 and C_2 were obtained by partial freezing and decantation of the liquid part; the solid was then broken up, stirred, and dried with filter-paper. C_3 was collected from the hard solid which first formed round the edge at the top.

The use of the analytical results in making the table is exemplified for sample C_1. 1·756 Grams of solid give 0·651 g. or 0·00822 gram-atom of selenium, which is equivalent to 0·915 gram of the dioxide. The difference in weight between the original substance and the dioxide, *i.e.*, 1·756—0·915, is taken as the quantity of hydrogen fluoride (gravimetric) and is 0·04205 mol. The molar ratio of hydrogen fluoride (gravimetric by difference) to selenium dioxide (gravimetric) is therefore 0·04205/0·00822 = 5·1. 1·756 Grams of solid require 58·58 c.c. of 0·988 *N*-alkali, with thymolphthalein as indicator. By subtracting from the total milliequivalents of acid, *i.e.*, 57·66, the equivalents of selenious acid, *i.e.*, 0·01645, the equivalent of hydrogen fluoride is found to be 0·0412. The ratio hydrogen fluoride (volumetric by difference) to selenium dioxide (gravimetric) is 5·0.

The weight of hydrogen fluoride so found (volumetric by difference), *i.e.*, 0·824 g., when added to the selenium dioxide, 0·918 g., gives the weight of product calculated from the volumetric total acid and gravimetric selenium; *i.e.*, 1·739. These are the values in brackets in column 2.

Description of preparation and sample.	Wt. taken. Wt. calc. from analysis in brackets.	Ratio nHF/SeO_2 from gravimetric selenium and total wt. of sample.	Ratio nHF/SeO_2 from gravimetric selenium and total acid found.
Distillate at 85° and over (p. 168).	0·5435 (0·507)	14·65	12·85
B_1. Solid sucked dry on cooled Gooch.	0·5405 (0·5124)	4·5	4·5
B_2. Solid dried by pressing on Gooch.	3·56 (3·47)	4·93	4·94
B_3. Solid washed with cold chloroform.	1·236 (1·170)	5·3	4·8
C_1. Solid, first fraction dried with filter-paper.	1·756 (1·739)	5·15	5·0
C_2. Solid, second fraction.	0·984 (0·998)	4·55	4·45
C_3. Solid first formed on surface.	0·6695 (0·664)	—	(4·9) Corrected volumetric as on p. 170.
C_4. Liquid, mother-liquor of C_1 and C_2.	2·770 2·83	4·14	4·34

Summary and Conclusions.

The analyses show that the solid frozen out of our liquid product contains constantly about 5 mols. of hydrogen fluoride to 1 mol. of selenium dioxide. The fluctuations are, we consider, due to inclusion of mother-liquor, to the loss of variable quantities of hydrogen fluoride, and to other difficulties inherent in the analysis of so corrosive a substance. This additive compound, $SeO_2,5HF$, is in equilibrium with liquids of various compositions. It dissociates in the vapour phase, giving off small quantities of hydrogen fluoride, the vapour pressure of which is only a small fraction of that of the pure acid. At higher vapour pressures the dissociation of the vapour which contains selenium dioxide is not complete. Thus the same compound is obtained either by distillation of the excess of hydrogen fluoride or by freezing from liquids of different compositions.

The above is one of the few examples of complex formation between hydrogen fluoride and an acid anhydride. Analogous compounds with tellurous anhydride have been prepared by Metzner (*Ann. Chim. Phys.*, 1898, **15**). These were prepared from aqueous hydrogen fluoride. One of them was much hydrated; $2TeF_4,3TeO_2,6H_2O$. The other, given as $TeF_4,TeO_2,2H_2O$, might of course be written as $2TeO_2,4HF$. We have prepared a compound somewhat similar to this from anhydrous hydrogen fluoride which we hope to describe in a later communication. The probabilities of the two formulæ are evenly balanced in the case of tellurium, but in the case of selenium we consider the latter, or additive compound, formula far more probable. The fluoride of so strongly electronegative an element is probably not formed under conditions which involve elimination of water, or at any rate, if there is some anhydrous fluoride in the presence of a large excess of hydrogen fluoride, it would be very difficult to prove its presence and isolate it. Up to the present, no fluorides or oxyfluorides of quadrivalent selenium have been described, with the important exception of the compound, afterwards claimed to be the hexafluoride, described by Lebeau (*Compt. rend.*, 1906, **144**, 1042). His first preparation, the analysis of which corresponded to SeF_4, had the properties to be expected and also resembled our present compound. It was a colourless liquid, boiling at about $+100°$, and solidifying at $-80°$. It decomposed water, giving hydrofluoric and selenious acids in the molar ratio 4 : 1.

A comparison between the actions of hydrogen fluoride and hydrogen chloride on selenium dioxide is instructive. Hydrogen chloride also gives in the first place an additive compound, which, however, easily loses water, giving the oxychloride $SeOCl_2$ (Lenher, *J. Amer. Chem. Soc.*, 1920, **42**, 2498). Loss of water from our

compound did not take place under the conditions tried and is unlikely in the case of the compound obtained from hydrogen fluoride on account of the order of the affinities of fluorine and oxygen for hydrogen.

The apparatus required in the preparation of the hydrogen fluoride, and the platinum used in the manipulation of the products were obtained by means of a grant from the Royal Society, which is gratefully acknowledged. The selenium was kindly presented by the Baltimore Copper Company.

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UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, August 24th*, 1925.]

XXVIII.—*The Hydration of Strong Electrolytes, the Viscosity of their Aqueous Solutions, and the Dilution Law.*

By JAMES NETHERWOOD SUGDEN.

MANY attempts have been made to determine the hydration of strong electrolytes in aqueous solution. The results of different methods of investigation differ widely, some yielding relatively small hydration numbers, up to 20 molecules of water per molecule of a hydrated salt, whereas others give much larger values which are quoted in many text-books (*e.g.*, Nernst's "Theoretical Chemistry," 1923, p. 450; Freundlich, "Kapillarchemie," 1923, p. 81). In consequence of this uncertainty, it has not hitherto been possible to apply a hydrate theory to those properties of salt solutions which may be expected to depend on the hydration of the solute. An attempt has been made in this paper to apply, in a quantitative way, a new hydrate theory which is put forward as a result of the experimental work outlined in subsequent sections.

Determination of Hydration Numbers.

It has been shown by Frazer and Myrick (*J. Amer. Chem. Soc.*, 1916, **38**, 1907), Scatchard (*ibid.*, 1921, **43**, 2406), and Washburn (*Tech. Quart.*, 1908, **21**, 373), from the osmotic pressure, vapour pressure, and freezing-point depression respectively, that at moderate temperatures and at concentrations as high as molar, sucrose behaves as if it formed a hexahydrate in solution, and this fact forms a convenient starting point for testing other methods which are applicable both to electrolytes and to non-electrolytes. One such method was indicated by Philip (*Trans. Faraday Soc.*, 1907, **3**, 1),

who recalculated the experimental results of Knopp (*Z. physikal. Chem.*, 1904, **48**, 97), Steiner (*Wied. Ann.*, 1894, **52**, 275), and Muller (*Z. physikal. Chem.*, 1912, **81**, 483) on the solubility of gases in aqueous solutions of sucrose, potassium chloride, etc., and showed that the solubility of hydrogen, nitrogen, and oxygen in these solutions was considerably less than might be expected from their known water content. He suggested that this lowering of solubility might be accounted for by assuming that some of the water was attached to the solute as water of hydration and thereby removed from its rôle of solvent, and that the lowering of solubility afforded a direct measure of this "fixed" water. Philip and Bramley (J., 1915, **107**, 377, 1831) employed the distribution method to measure this effect, while H. E. Armstrong and his collaborators (*Proc. Roy. Soc.*, 1906, **78**, *A*, 272; 1907, **79**, *A*, 576, 579, 586; 1908, **81**, *A*, 102; 1912, **87**, *A*, 582; J., 1911, **99**, 349, 371), by investigating the velocity of reactions such as the inversion of sucrose and the hydrolysis of methyl acetate by dilute acids, alone and in presence of their salts, calculated the hydration of the salt by estimating the amount of water required to be added to the solution in order to restore the velocity coefficient to its original value. In view of the approximate agreement of the results obtained by these methods, it was thought desirable to make a further study of the problem by the distribution method, which is the most convenient.

The experimental conditions desirable on theoretical grounds were laid down by Philip and Bramley (*loc. cit.*), but these have been modified in that a system was sought in which the distributed solute (*a*) can be estimated quickly, preferably by simple titration, (*b*) is miscible in all proportions with both the aqueous and the non-aqueous phase, and (*c*) is distributed equally between the two solvent phases. Only one such system could be found, *viz.*, acetic acid distributed between water and amyl alcohol, which had been investigated by Herz and Fischer (*Ber.*, 1904, **37**, 4746; 1905, **38**, 1138). The distribution coefficient was found to vary somewhat with the source of the alcohol (usually about the figure 0·96) and to be independent of the concentration of the acetic acid when tested on the following systems: amyl alcohol and (*a*) water, (*b*) 2*N*-sodium chloride, (*c*) *N*-potassium nitrate, (*d*) 0·25 *N*-sucrose, and also of the time, showing that esterification in the alcohol phase did not take place. The objections to this system are (*a*) the two solvents are slightly miscible with each other, (*b*) some salts are not insoluble in amyl alcohol, (*c*) iodides are decomposed by the acetic acid and the liberated iodine dissolves in the alcohol, and (*d*) acetic acid cannot be estimated by titration in presence of

ammonium salts. Complete immiscibility is, however, not essential when the distribution coefficient is approximately unity, and other methods can be applied in the case of the soluble lithium, magnesium, and calcium salts and of ammonium salts.

If d_1 and d_2, and C_1 and C_2, are respectively the densities and distribution coefficients of water and a salt solution of normality n, the total weight of water per litre of solution is $1000d_2 - nE$ (E being the equivalent weight of the salt). The weight of free water is taken to be $1000d_1 \cdot C_1/C_2$ ($d_1 = 0{\cdot}99707$), and consequently the weight of water attached to n gram-equivalents of the salt is $1000d_2 - nE - 1000d_1C_1/C_2$ and the apparent equivalent hydration

$$H = 1000(d_2 - C_1d_1/C_2)/18n - E/18.$$

This calculation assumes the solvents to be completely immiscible, the quantity of acetic acid (actually 1 c.c. of acid per 200 c.c. of solvents) to be negligible, and the indicating substance (acetic acid) to be insoluble in the salt whose hydration is being determined.

In Table I are the results of the first experiments, with sucrose. The apparent molecular hydration, H, increases with dilution until

TABLE I.

n.	d.	C_1.	C_2.	H.	n.	d.	C_1.	C_2.	H.
$2N$	1·2532	0·9870	2·061	2·7	$N/4$	1·0300	0·9227	1·019	5·0
		0·9625	2·030	2·7			0·9625	1·042	5·2
N	1·1270	0·9780	1·376	4·2	$N/5$	1·0234	0·9663	1·029	5·1
		0·9625	1·360	4·3			0·9663	1·030	5·6
$N/2$	1·0623	0·9625	1·135	5·2	$N/7$	1·0153	0·9663	1·011	5·5
		0·9628	1·133	4·9			0·9659	1·012	6·1
$N/3$	1·0407	0·9663	1·072	4·8	$N/10$	1·0103	0·9628	0·9933	5·6
		0·9659	1·073	4·9			0·9628	0·9954	6·5

a value of 5 to 6 molecules of water is obtained. The method of estimating H is by difference, and the experimental error increases rapidly as the fraction of "fixed" water decreases, *i.e.*, as the dilution increases; in the case of sucrose a steady value is not indicated until a dilution is reached where the experimental error becomes appreciable, nevertheless the average value so obtained is in good agreement with that deduced from the osmotic properties of sucrose solutions.

Table II gives the results obtained for all the salts investigated, and Table IIA summarises those for the alkali metals.

In every case except the sulphates, a reasonably constant value of H was obtained, usually over the range $N - N/10$. The values in the column headed H(ex.)* are those which might be ascribed

* Where the values of H over the range $N - N/4$ are reasonably constant, H (ex.) is taken as the average. Where H is large and the maximum value is not reached at normal concentration, *e.g.*, LiBr, $LiBrO_3$, less weight is attached to this determination.

TABLE II.

Conc. (*N.*).	d_2.	C_1.	C_2.	H.
		LiCl.		
1·516	1·0332	0·9526	1·2990	8·7
1·0	1·0214	0·9526	1·1714	9·3
0·5	1·0095	0·9526	1·0052	9·8
0·25	1·0034	0·9526	1·0006	9·75
0·1	0·9995	0·9526	0·9698	8·8
		NaCl.		
2·0	1·0794	0·9780	1·3660	6·9
1·0	1·0380	0·9424	1·1150	7·0
0·5	1·0180	0·9526	1·0331	8·0
0·25	1·0078	0·9600	1·0006	8·1
0·1	1·0013	0·9628	0·9759	6·5
		KCl.		
2·0	1·0872	0·9820	1·1940	3·3
1·0	1·0427	0·9600	1·0534	3·3
0·5	1·0206	0·9424	0·9868	3·5
0·25	1·0091	0·9600	0·9808	3·3
0·1	1·0019	0·9520	0·9605	3·3
		LiBr.		
1·232	1·0735	0·9410	1·1533	6·9
0·616	1·0353	0·9410	1·0504	8·1
0·308	1·0162	0·9410	0·9922	7·9
0·1232	1·0047	0·9410	0·9600	7·5
		NaBr.		
2·0	1·1503	0·9520	1·3024	6·0
1·0	1·0747	0·9520	1·1045	6·2
0·5	1·0360	0·9600	1·0343	6·4
0·25	1·0165	0·9526	0·9892	6·8
0·1	1·0045	0·9526	0·9663	6·3
		KBr.		
2·0	1·1623	0·9520	1·1030	1·8
1·0	1·0802	0·9520	1·0240	1·9
0·5	1·0394	0·9520	0·9861	1·9
0·25	1·0181	0·9520	0·9687	1·9
0·1	1·0052	0·9520	0·9582	1·5
		$LiNO_3$.		
0·900	1·0322	0·9410	1·0156	2·9
0·450	1·0147	0·9410	0·9820	3·5
0·225	1·0062	0·9410	0·9592	3·1
0·090	1·0006	0·9410	0·9478	2·8
		$NaNO_3$.		
2·0	1·1040	0·9526	1·1032	2·0
1·0	1·0518	0·9600	1·0266	1·9
0·5	1·0247	0·9526	0·9815	1·6
0·25	1·0113	0·9600	0·9740	1·6
0·1	1·0028	0·9600	0·9625	1·6
		KNO_3.		
1·0	1·0574	0·9600	0·9581	−2·4
0·5	1·0276	0·9600	0·9559	−2·6
0·25	1·0131	0·9520	0·9497	−2·6
0·125	1·0044	0·9520	0·9506	−3·0
		$NaClO_3$.		
2·0	1·1335	0·9632	1·2150	3·6
1·0	1·0662	0·9632	1·0758	3·7
0·5	1·0319	0·9632	0·9736	3·7
0·25	1·0148	0·9632	0·9880	3·7
0·1	1·0044	0·9632	0·9716	2·9
		$KClO_3$.		
0·25	1·0161	0·9526	0·9585	−1·2
0·1	1·0048	0·9526	0·9554	−0·9

Conc. (*N.*).	d_2.	C_1.	C_2.	H.
		$LiBrO_3$.		
0·830	1·0809	0·9412	1·0962	7·5
0·415	1·0392	0·9412	1·0143	7·75
0·2075	1·0180	0·9412	0·9774	7·95
0·083	1·0058	0·9412	0·9527	6·4
		$NaBrO_3$.		
1·0	1·1122	0·9632	1·1350	6·4
0·5	1·0550	0·9632	1·0437	6·6
0·25	1·0260	0·9632	1·0021	6·6
0·1	1·0089	0·9632	0·9770	6·0
		$KBrO_3$.		
0·25	1·0290	0·9227	0·9405	2·0
		$LiIO_3$.		
0·9927	1·1506	0·9227	1·1106	7·9
0·4963	1·0745	0·9412	1·0241	7·6
0·2482	1·0360	0·9227	0·9613	7·6
0·0993	1·0127	0·9227	0·9393	8·5
		$NaIO_3$.		
0·25	1·0400	0·9412	0·9700	5·1
0·1	1·0141	0·9510	0·9616	4·5
		KIO_3.		
0·25	1·0414	0·9227	0·9376	1·5
		$\frac{1}{2}Na_2SO_4$.		
2·0	1·1150	0·9780	1·4160	7·9
1·0	1·0572	0·9780	1·1370	7·2
0·5	1·0283	0·9410	1·0020	6·3
0·25	1·0134	0·9410	0·9650	5·2
0·1	1·0043	0·9410	0·9443	2·0
		$\frac{1}{2}K_2SO_4$.		
1·0	1·0638	0·9780	1·0570	3·0
0·5	1·0310	0·9410	0·9661	1·8
0·25	1·0137	0·9410	0·9491	0·8
		$MgCl_2$.		
2·260	1·0790	0·9424	1·4567	16·0
1·130	1·0389	0·9424	1·1983	19·6
0·565	1·0183	0·9424	1·0632	21·0
0·2825	1·0077	0·9424	0·9998	19·4
0·113	1·0013	0·9424	0·9615	18·4
		$CaCl_2$.		
2·186	1·0924	0·9510	1·4374	15·8
1·093	1·0458	0·9510	1·1804	18·6
0·546	1·0216	0·9400	1·0403	18·4
0·273	1·0095	0·9510	1·0050	18·9
0·109	1·0020	0·9510	0·9735	22·4
		$SrCl_2$.		
2·0	1·1369	0·9510	1·4052	15·8
1·0	1·0679	0·9510	1·1690	18·6
0·5	1·0320	0·9510	1·0514	19·0
0·25	1·0150	0·9510	0·9980	18·8
0·1	1·0044	0·9510	0·9713	21·9
		$BaCl_2$.		
2·0	1·1740	0·9632	1·3323	13·6
1·0	1·0869	0·9600	1·1387	15·8
0·5	1·0424	0·9780	1·0630	16·2
0·25	1·0198	0·9632	1·0036	16·3
0·1	1·0062	0·9632	0·9760	13·1
		$MgBr_2$.		
1·7624	1·1302	0·9227	1·2845	15·9
0·8812	1·0641	0·9227	1·0960	18·2
0·4406	1·0308	0·9227	1·0090	19·8
0·2203	1·0140	0·9227	0·9623	19·0
0·0881	1·0040	0·9227	0·9402	21·6

TABLE II (*continued*).

Conc. (*N*.)	d_2.	C_1.	C_2.	*H*.	Conc. (*N*.)	d_2.	C_1.	C_2.	*H*.
		$CaBr_2$.					$Ca(NO_3)_2$.		
2·148	1·1706	0·9424	1·3282	12·8	2·18	1·1243	0·9400	1·1448	6·5
1·074	1·0848	0·9424	1·1323	15·3	1·09	1·0618	0·9400	1·0346	6·8
0·537	1·0412	0·9424	1·0365	16·8	0·545	1·0292	0·9400	0·9850	6·7
0·268	1·0193	0·9424	0·9857	16·2	0·2725	1·0130	0·9400	0·9619	6·7
0·1074	1·0063	0·9424	0·9603	17·9	0·109	1·0036	0·9400	0·9480	6·2
		$SrBr_2$.					$Sr(NO_3)_2$.		
2·0	1·2027	0·9400	1·2737	12·2	1·9736	1·1297	0·9510	1·1495	5·4
1·0	1·1008	0·9400	1·1011	14·0	0·9868	1·0775	0·9510	1·0373	6·7
0·5	1·0493	0·9424	1·0264	16·0	0·4939	1·0377	0·9510	0·9923	6·8
0·25	1·0231	0·9400	0·9795	15·7	0·2969	1·0176	0·9510	0·9715	7·0
0·1	1·0078	0·9400	0·9536	14·0	0·09868	1·0057	0·9510	0·9578	6·0
		$BaBr_2$.					$Ba(NO_3)_2$.		
2·0	1·2510	0·9424	1·2400	10·9	0·5	1·0494	0·9510	0·9825	4·2
1·0	1·1251	0·9424	1·0900	12·7	0·25	1·0233	0·9510	0·9660	4·0
0·5	1·0615	0·9424	1·0146	13·6	0·1	1·0076	0·9510	0·9565	3·5
0·25	1·0293	0·9424	0·9777	13·4			$MgSO_4$.		
0·1	1·0100	0·9424	0·9572	15·0	2·0	1·1104	0·9400	1·4855	20·0
		$Mg(NO_3)_2$.			1·0	1·0552	0·9400	1·1555	20·4
2·02	1·0993	0·9400	1·1448	7·2	0·5	1·0266	0·9400	1·0287	19·0
1·01	1·0489	0·9400	1·0394	8·0	0·25	1·0121	0·9400	0·9788	17·6
0·505	1·0231	0·9400	0·9889	8·3	0·1	1·0035	0·9400	0·9519	14·4
0·2525	1·0100	0·9400	0·9634	8·1					
0·101	1·0023	0·9400	0·9467	5·3					

to the salt from these experimental results alone, whilst under *H* are the most probable values for the apparent molecular hydration. Where the values in the two columns differ, the explanation is usually to be found in the solubility of the salt in the alcohol phase; the evidence upon which the final figure is based will appear in later sections. All previous work on hydration suggests that this

TABLE IIA.

Salt.	2*N*.	*N*.	*N*/2.	*N*/4.	*N*/10.	*H* (ex.).*	*H*.
LiCl	8·7	9·3	9·8	9·75	8·8	9·8	10·5
NaCl	6·9	7·6	8·0	8·1	6·5	8·0	7·9
KCl	3·3	3·3	3·5	3·3	3·3	3·4	3·4
LiBr	—	6·9	8·1	7·9	7·5	8·0	9·0
NaBr	6·0	6·2	6·4	6·8	6·3	6·6	6·4
KBr	1·8	1·9	1·9	1·9	1·5	1·9	1·9
$LiNO_3$	—	2·9	3·5	3·1	2·8	3·4	4·4
$NaNO_3$	2·0	1·9	1·6	1·6	1·6	1·8	1·8
KNO_3	—	−2·4	−2·6	−2·6	−3·0	−2·6	−2·7
$LiClO_3$	—	—	—	—	—	—	6·3
$NaClO_3$	3·6	3·7	3·7	3·7	2·9	3·7	3·7
$KClO_3$	—	—	—	−1·2	−0·9	−1·0	−0·8
$LiBrO_3$	—	7·5	7·75	7·95	6·4	7·8	9·2
$NaBrO_3$	—	6·4	6·6	6·6	6·0	6·6	6·6
$KBrO_3$	—	—	—	2·0	—	2·0	2·1
$LiIO_3$	—	7·9	7·6	7·6	8·5	7·7	7·7
$NaIO_3$	—	—	—	5·1	4·5	5·1	5·1
KIO_3	—	—	—	1·5	—	1·5	0·6
$\frac{1}{2}Na_2SO_4$	7·9	7·2	6·3	5·2	2·0	—	—
$\frac{1}{2}K_2SO_4$	—	3·0	1·8	0·8	—	—	—

quantity is not independent of the salt concentration, but the results now obtained (with the one exception) do not support this view, and, whilst it cannot be shown from them alone whether or not the constant value is retained as the dilution is still further increased, it will be convenient, for the time being, to regard these as fixed values. The sulphates are anomalous, the values of H actually decreasing on dilution. This may be due to the appearance and subsequent dissociation of intermediate ions of the type KSO_4, or to some idiosyncrasy of the sulphate ion; salts of the type $BaCl_2$ and $Sr(NO_3)_2$ behave in the normal way.

Potassium bromate and iodate are only sparingly soluble salts, consequently their hydration could not be determined with accuracy. Potassium nitrate and potassium chlorate both gave constant *negative* values for H. Analysis of the figures brings out the interesting fact that *the difference between the apparent molecular hydration of a sodium and a potassium salt is independent of the anion, hydration thus being an additive property* (Table III).

TABLE III.

	Cl.	Br.	NO_3.	ClO_3.	BrO_3.	IO_3.
Na	8·0	6·6	1·8	3·7	6·6	5·1
K	3·4	1·9	−2·6	−1·0	2·0	(1·5)
Diff.	4·6	4·7	4·4	4·7	4·6	(3·6)

The average value for the Na–K difference is 4·6 mols. H_2O. The determination of the corresponding Li–Na difference presented some difficulty, due to the solubility of lithium salts in amyl alcohol. Of those examined, the iodate alone was insoluble, so the difference (2·6 mols. H_2O) depends on only one determination; moreover, sodium iodate is a sparingly soluble salt and the most concentrated solution available was $N/4$, hence the value $H = 5·1$ for this salt is not known with the usual accuracy. Nevertheless, the difference value of 2·6 is probably not greatly in error; the hydration values for the other lithium salts tabulated in column H (Table II) are obtained by adding 2·6 to the hydration number of the corresponding sodium salts.

Table IV gives a summary of the values of H for the salts of the alkaline earths. The magnesium and calcium salts dissolved in the amyl alcohol and in each case the numbers in column H (ex.) are too small, but good values were obtained for the strontium and barium salts; the chlorides and bromides are heavily hydrated and hence the maximum value is in some cases not obtained until a dilution somewhat greater than normal is reached.

Table V indicates that hydration is additive in these salts also, and Table VI that the chloride–nitrate difference is common to both series.

TABLE IV.

Salt.	2*N*.	*N*.	*N*/2.	*N*/4.	*N*/10.	*H* (ex.).	*H*.
$MgCl_2$	16·0	19·6	21·0	19·4	18·4	20·0	24·8
$CaCl_2$	15·8	18·6	18·4	18·9	22·4	18·4	20·6
$SrCl_2$	15·8	18·6	19·0	18·8	21·9	18·8	18·8
$BaCl_2$	13·6	15·8	16·2	16·3	13·1	16·2	16·2
$MgBr_2$	15·9	18·2	19·8	19·0	21·6	19·2	21·8
$CaBr_2$	12·8	15·3	16·8	16·2	17·9	16·3	17·6
$SrBr_2$	12·2	14·0	16·0	15·7	14·0	15·9	15·8
$BaBr_2$	10·9	12·7	13·6	13·4	15·0	13·5	13·2
$Mg(NO_3)_2$	7·2	8·0	8·3	8·1	5·3	8·1	12·8
$Ca(NO_3)_2$	6·5	6·8	6·7	6·7	6·2	6·75	8·6
$Sr(NO_3)_2$	5·4	6·7	6·8	7·0	6·0	6·7	6·8
$Ba(NO_3)_2$	—	—	4·2	4·0	3·5	4·1	4·1
$MgSO_4$	20·0	20·4	19·0	17·6	14·4	—	—

TABLE V.

	Cl.	Br.	NO_3.
Sr	18·8	15·9	6·7
Ba	16·2	13·5	4·1
Diff.	2·4	2·4	2·6

TABLE VI.

	Na.	K.	½Sr.	½Ba.
Cl	8·0	3·4	9·4	8·1
NO_3	1·8	−2·6	3·35	2·05
Diff.	6·2	6·0	6·05	6·05

Negative Hydration.

The salts possessing negative hydration values are the chlorates and nitrates of potassium and presumably also of ammonium, rubidium, and cæsium. Since, so far as the additive nature of hydration is concerned, these salts are apparently normal, it is probable that this phenomenon is not an abnormality, but merely an extreme example of some property common to all strong electrolytes. In this particular case, the negative hydration is indicated by the fact that solutions of these salts exert a greater solvent power upon acetic acid than does pure water. An obvious explanation is that some measure of combination takes place between the salt and acetic acid, but several arguments may be raised against this. One of these (and others will appear later) is that the negative hydration, or, from the point of view of this explanation, the extent of combination between the two substances is independent of the concentration of both the potassium nitrate and the acetic acid over a wide range of concentration. The increased solvent power of potassium nitrate solutions is not confined to acetic acid alone; reference to the papers of Rothmund (*Z. physikal. Chem.*, 1900, **33**, 401), Biltz (*ibid.*, 1903, **43**, 41), Bray and Winninghoff (*J. Amer. Chem. Soc.*, 1911, **33**, 1663), and Glasstone and Saunders (J., 1923, **123**, 2134) shows that the property extends over a very wide range of compounds, including the particularly interesting case of lead nitrate (Glasstone and Saunders), which contains a common ion. Moreover, whereas the ordinary process

of hydration produces a concentrating effect upon other constituents of an aqueous solution, evidence is not lacking that these " negatively hydrated " salts actually produce a *diluting effect*, a property which has been noticed by Rennie, Higgin, and Cooke (J., 1908, **93**, 1162), Armstrong and Watson (*Proc. Roy. Soc.*, 1907, **79**, *A*, 586), Harned (*J. Amer. Chem. Soc.*, 1918, **40**, 1461), and Walton (*Z. physikal. Chem.*, 1904, **47**, 185).

Several explanations of these anomalies are to be found in the above papers, but in seeking a general interpretation which will cover these and other properties of solutions of strong electrolytes the possibility was considered that the anions and kations might react with the solvent in fundamentally different ways. All the published work on hydration of strong electrolytes agrees on two points: (1) if kations are arranged in the order of diminishing hydration, the cæsium ion occupies the lowest position, and (2) if the anions are so arranged, the chloride ion occupies the position of maximum hydration; this, together with the definite proof advanced by Washburn (*J. Amer. Chem. Soc.*, 1915, **37**, 694) that the least hydrated kation (cæsium) carries measurably more water than the (presumably) most heavily hydrated anion (chloride), suggests at once that anions are not hydrated, but possess properties which in certain cases are sufficiently developed to overcompensate the hydration effect of the kation.

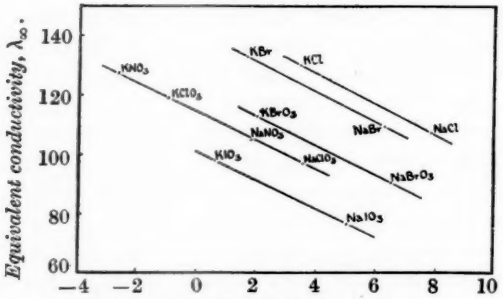
When acetic acid is in equilibrium both with water and with amyl alcohol, its activity in each phase must be the same, and (if the solution is sufficiently dilute) proportional to its mole-fraction, which in the aqueous phase is assumed to depend on the " association factor " of water. If the mole-fraction (activity) of the acetic acid in the aqueous phase is increased by the removal of water as water of hydration, some of the acid will escape into the alcohol phase until equilibrium is re-established. Alternatively, if the association factor of water is decreased by any means whatsoever, the mole-fraction of the acetic acid will decrease and can only be restored by transference of the acid from the alcohol to the water phase. The suggestion is made, therefore, that whilst kations are invariably hydrated, probably as a result of the positive field (the intensity of which decreases as the ionic radius increases) round the ion and a stray field round the water molecule, anions are not hydrated but in all cases exert (in greater or less degree) a depolymerising action on the associated solvent, resulting in a shift of the equilibrium $(H_2O)_3 \rightleftarrows (H_2O)_2 + H_2O \rightleftarrows 3H_2O$ towards the right. The properties of solutions of strong electrolytes are thus to a large degree determined by the relative magnitudes of these two rival processes.

An action such as the above, which increases the effective mole-fraction of the water, will produce a species of water molecule which alone is found in the vapour phase; hence aqueous solutions of negatively hydrated salts should have abnormally high vapour pressures (compare Washburn, *J. Amer. Chem. Soc.*, 1910, **32**, 653, 1636; Washburn and MacInnes, *ibid.*, 1911, **33**, 1686; Bousfield, *Trans. Faraday Soc.*, 1919, **15**, 47; Glasstone and Saunders, *loc. cit.*; Sidgwick and Ewbank, J., 1924, **125**, 2273).

Hydration and the Equivalent Conductivity at Infinite Dilution.

Kohlrausch (*Proc. Roy. Soc.*, 1903, **71**, *A*, 348) suggested that "about every ion moves an atmosphere of the solvent the dimensions of which are determined by the characteristics of the ion,

FIG. 1.



and the electrolytic resistance of an ion is a frictional resistance that increases with the dimension of the atmosphere"; consequently a quantitative relationship may be expected between λ_∞ and the hydration of the kations.* In order to correlate these properties, let it be assumed that H is independent of concentration up to infinite dilution. This assumption is not unreasonable in view of the facts presented in this paper, and further, it leads to conclusions which are supported by considerations based on the constancy of H over the experimental range $N - N/10$ only.

If the apparent molecular hydrations of the alkali chlorides are plotted against the equivalent conductivities at infinite dilution, the points lie on a smooth curve, which is slightly concave towards the origin. The shape of the curve is determined by the properties (λ_∞ and H) of the kations, and its position on the diagram by the equivalent conductivity of the anion. In a similar diagram drawn for the salts of a common kation, the points lie irregularly

* The hypothesis cannot be true universally if anions are not hydrated.

and can only be joined by a zig-zag line. This dissimilarity supports the hypothesis that anions and kations behave towards the solvent in different ways.

The curvature of the lines relating λ_∞ and H for the alkali metals (so far as their hydrations are known) is so slight that the purpose of the diagram is served equally well by plotting the values for the sodium and potassium salts only and joining the points by straight lines (Fig. 1). Two points of interest, which will be encountered again later, become evident: (*a*) the nitrates and chlorates fall on one line, and (*b*) the sequence of the curves for the bromates, chlorates, and iodates is unexpected.

Hydration of Strong Electrolytes and the Viscosity of their Aqueous Solutions.

Strong electrolytes may be divided into two classes according to their effect on the viscosity of water. The first (and smaller) class consists of the salts of the heavier alkali metals the aqueous solutions of which at the ordinary temperature have viscosities lower than that of the solvent. With increasing concentration, the viscosity falls at first to a minimum and then increases to a value which, in the case of very soluble salts, may exceed the viscosity of water. At higher temperatures the minimum becomes less marked and finally disappears, the solution then behaving as solutions of electrolytes of the second (and larger) class, the viscosities of which are always greater than that of water.

Many unsatisfactory and conflicting theories have been put forward to explain the negative viscosity ($\eta/\eta_0 - 1$ being negative) of some salt solutions, *e.g.*, by Euler (*Z. physikal. Chem.*, **1898**, **25**, 536), Wagner (*ibid.*, 1903, **46**, 871), Jones and Veazey (*Amer. Chem. J.*, 1907, **37**, 405), and Taylor (*Proc. Roy. Soc. Edin.*, 1907, **28**, 461).

Getman (*J. Chim. Phys.*, 1907, **5**, 344; *J. Amer. Chem. Soc.*, 1908, **30**, 721, 1077) ascribed negative viscosity at least partly to association of the solvent (potassium iodide in non-associated solvents having a positive viscosity), Bousfield (J., 1915, **107**, 1797) pointed out that "the viscosity of dilute aqueous solutions cannot be theoretically treated except in conjunction with the effect of the peculiar constitution of water," and Rabinowitsch (*J. Amer. Chem. Soc.*, 1922, **44**, 954) showed, from theoretical considerations, that whilst hydration of ions can account for an increased viscosity, depolymerisation of the solvent alone supplies a rational explanation of the negative viscosity of some salt solutions.

When the kation is only slightly hydrated and the non-hydrated anion is small, or efficient in depolymerising the solvent, the effect

of the anion predominates, and the viscosity of the solution will be negative; but with increasing salt concentration, and therefore increasing depolymerisation, the average size of the water molecules becomes smaller, and hence the tendency of the kation to increase the viscosity will become more marked, eventually accounting for the minimum value and subsequent increase in the viscosity. Increase of temperature causes depolymerisation and consequently the disappearance of the minimum in the curve, the solvent functioning at higher temperatures as if it consisted only of simple molecules or complexes incapable of easy depolymerisation.

FIG. 2.

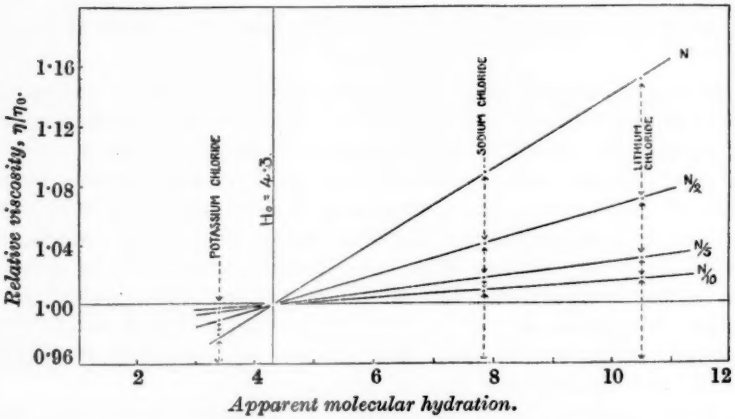


Fig. 2 shows the relation between the hydration of the alkali chlorides and the relative viscosity * of their solutions. If the latter is greater than unity, it is at all concentrations a linear function of the apparent molecular hydration of the salt; if less than unity, this relationship holds up to approximately semi-normal concentration. The straight lines in Fig. 2 all pass through a point where $\eta/\eta_0 = 1$ and $H = 4·3$. If an alkali chloride had this hydration value of 4·3, all disturbing influences would exactly compensate one another and the viscosity of its solutions at all concentrations would be the same as that of pure water. The relative viscosities of solutions of the alkali chlorides are proportional to the differences between their apparent molecular hydrations and this "zero" value, which may be denoted by H_0. The point of origin $\eta/\eta_0 = 1$, $H = 4·3$ is independent both of the concen-

* Except where otherwise stated, the accurate viscosity measurements of Grüneisen (*Wiss. Abhandl. Physikal.-Tech. Reichsanst.*, 1905, **4**, 239), and the collected data of Noyes and Falk (*J. Amer. Chem. Soc.*, 1912, **34**, 463) have been used.

tration and of the nature of the kation; it is determined by the anion, of which it is a specific property. The viscosities of these solutions depend, therefore, on (*a*) the value of H_0, which is fixed by the anion, (*b*) the hydration of the salt (determined largely by the kation), and (*c*) the concentration of the solution.

Many empirical equations have been proposed connecting the viscosities and the concentrations of solutions of strong electrolytes. The simplest of these (Arrhenius, *Z. physikal. Chem.*, 1887, **1**, 284),

$$\log \eta/\eta_0 = \theta c \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where θ is a constant varying from salt to salt and c is the number of gram-molecules per litre, holds with considerable accuracy over a wide range of concentrations, provided the solutions are more viscous than water, whilst for solutions of negative viscosity its application is limited tc dilutions greater than semi-normal. It is obvious from Fig. 2 that the constant θ may be expressed in terms of the apparent molecular hydration, H, and a more general constant, K:

$$\theta = K(H - H_0) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

whence

$$\log \eta/\eta_0 = Kc(H - H_0) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

a general equation which has the same applicability as that of Arrhenius. In Table VII, K is evaluated for the alkali chlorides, the calculated values of η/η_0 being then obtained from the equation

$$\log \eta/\eta_0 = 0{\cdot}01c(H - 4{\cdot}3) \quad . \quad . \quad . \quad . \quad (4)$$

TABLE VII.

	LiCl. $H = 10{\cdot}5$.			NaCl. $H = 7{\cdot}9$.			KCl. $H = 3{\cdot}4$.		
c.	η/η_0.	K.	η/η_0 (calc.).	η/η_0.	K.	η/η_0 (calc.).	η/η_0.	K.	η/η_0 (calc.).
1·0N	1·150	0·0098	1·153	1·086	0·0101	1·085	0·9820	(0·0088)	0·9785
0·5N	1·072	0·0097	1·074	1·041	0·0099	1·042	0·9898	0·0097	0·9897
0·2N	1·031	0·0107	1·029	1·0167	0·0101	1·0164	0·9959	0·0097	0·9958
0·1N	1·016	0·0111	1·014	1·0086	0·0103	1·0082	0·9982	0·0097	0·9989
0·05N	1·008	0·0109	1·007	1·0046	0·0110	1·004	0·9991	0·0096	0·9998

Mean value of $K = 0{\cdot}01$.

The figures in brackets in Tables VII and VIII refer to solutions for which $\eta/\eta_0 - 1$ is negative, and of such concentrations that equation (1) is no longer applicable.

The corresponding diagram for the alkali nitrates closely resembles that for the chlorides, except that the origin of the curves has shifted to the value $H_0 = 0$; however, the value of K (0·01) is the same (within the limits of experimental error), as will be seen from Table VIII.

TABLE VIII.

	$LiNO_3$. $H = 4{\cdot}4$.			$NaNO_3$. $H = 1{\cdot}8$.			KNO_3. $H = -2{\cdot}7$.		
c.	η/η_0.	K.	η/η_0 (calc.).	η/η_0	K.	η/η_0 (calc.).	η/η_0.	K.	η/η_0 (calc.).
$1{\cdot}0N$	1·1020	0·0094	1·1066	1·0540	0·0127	1·0423	0·9620	(0·0070)	0·9397
$0{\cdot}5N$	1·0503	0·0095	1·0520	1·0219	0·0104	1·0209	0·9754	(0·0083)	0·9694
$0{\cdot}2N$	1·0200	0·0096	1·0205	1·0082	0·0096	1·0084	0·9883	0·0095	0·9876
$0{\cdot}1N$	1·0112	0·0107	1·0102	1·0044	0·0102	1·0039	0·9841	0·0094	0·9969

It is possible, therefore, that K may be a universal constant and the equation

$$\log \eta/\eta_0 = 0{\cdot}01c(H - H_0) \quad . \quad . \quad . \quad . \quad (5)$$

a general one.

For the alkali iodates, which (with the exception of the lithium salt) are only sparingly soluble in water, the value of H_0 (Table IX) has been calculated from equation (5) instead of being obtained by the graphical method. The average value is — 5·5.

TABLE IX.

	c.	η/η_0.	H_0.	η/η_0 (calc.).
$LiIO_3$	$1{\cdot}00N$	1·3380	−4·9	1·3552
	$0{\cdot}20N$	1·0620	−5·4	1·0627
	$0{\cdot}05N$	1·0158	−5·7	1·0153
	$0{\cdot}025N$	1·0086	−6·7	1·0076
$NaIO_3$	$0{\cdot}20N$	1·0496	−5·4	1·0481
KIO_3	$0{\cdot}20N$	1·0270	−5·2	1·0285

The negative sign probably indicates that the iodate ion is sufficiently large of itself to increase the viscosity of water, an effect which is, of course, independent of its depolymerising action.

The values of H_0 for the bromides (4·1) and chlorates (0·0) were similarly found. In the case of the bromates, owing to lack of data, new viscosity measurements were made ($H_0 = 1{\cdot}6$).

TABLE X.

	$LiBrO_3$. $H = 9{\cdot}2$.				$NaBrO_3$. $H = 6{\cdot}6$.		
c.	η/η_0.	H_0.	η/η_0 (calc.).	c.	η/η_0.	H_0.	η/η_0 (calc.).
$0{\cdot}830N$	1·154	1·7	1·156	$1{\cdot}0N$	1·122	1·6	1·122
$0{\cdot}415N$	1·076	1·6	1·075	$0{\cdot}5N$	1·059	1·6	1·058
$0{\cdot}207N$	1·036	1·8	1·037	$0{\cdot}25N$	1·027	2·0	1·029
$0{\cdot}083N$	1·014	1·5	1·015	$0{\cdot}1N$	1·013	1·0	1·012

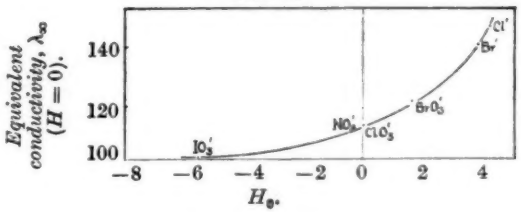
The values of H_0 thus found are 4·3 for Cl, 4·1 for Br, 1·6 for BrO_3, 0·0 for NO_3, 0·0 for ClO_3, and — 5·5 for IO_3. The chlorates and nitrates form one system here as in Fig. 1 and the sequence of the curves in Fig. 1 is that of these H_0 values. Fig. 3 shows the relation between the spacing of the curves in Fig. 1 as measured by the

value of λ_∞ at $H = 0$, and the values of H_0. This curve can be accurately described by the empirical equation

$$\lambda_\infty = 100 + 13{\cdot}5 \times 1{\cdot}327^{H_0} \quad . \quad . \quad . \quad . \quad (6)$$

It indicates a lower limit for the position of the curves in Fig. 1, only slightly below that of the iodate curve. Moreover, the smooth curve in Fig. 3 is of some importance, for whereas the values of H_0 are obtained from the viscosities of solutions over a concentration range similar to that available for the determination of hydration by the distribution method, the sequence and spacing of the curves in Fig. 1 depend on the application of these hydration values at infinite dilution. Fig. 3 therefore supplies some justification for extending the use of these hydration numbers to infinitely dilute solutions, since no serious error is thereby introduced. It must be mentioned, however, that " the viscosity concentration curve for all salts has a change of curvature at the dilute end in

FIG. 3.



the sense that the first particles of salt added have a greater effect in increasing, or a less effect in diminishing the viscosity of water than subsequent additions. The change in curvature is scarcely noticeable unless the curve is plotted on a large scale " (Applebey, J., 1910, **97**, 2000; see also Grüneisen, *loc. cit.*).

Salts of the type $BaCl_2$ can be treated in exactly the same way as those of the type KCl. By substituting the viscosity and apparent molecular hydration of barium chloride in equation (5), the value $H_0 = 7{\cdot}4$ is obtained. On the assumption that H_0 is determined solely by the anion the value for a bivalent chloride might be expected to be 8·6. The agreement, therefore, is not unsatisfactory, and supports the assumption that K in equation (5) is a universal constant.*

* It appears not unlikely that the size of a (unhydrated) kation is less than that of an average water molecule; consequently some small part of the water of hydration may be needed to adjust this difference, whilst the remainder tends to increase the viscosity of salt solutions. Hence H_0 for a bivalent chloride might be expected to be slightly less than twice the value for a univalent chloride, since, although the number of anions per molecule is doubled, that of the kations remains the same.

Having obtained H_0 for these salts, it is possible to calculate, from the equation

$$\log \eta/\eta_0 = 0{\cdot}01c(H - 7{\cdot}4) \quad . \quad . \quad . \quad . \quad (7)$$

the values of H for magnesium chloride ($H = 24{\cdot}8$) and calcium chloride ($H = 20{\cdot}6$). Where the final value of H differs from the experimental value H (ex.), (*i.e.*, for soluble salts), it is obtained (*a*) in Table IIA, from the additive property of hydration and (*b*) in Table IV, from this semi-empirical hydration–viscosity equation.

Hydration of Strong Electrolytes and the Dilution Law.

According to the theory here developed, the apparent molecular hydration, H, which represents the resultant of two opposing factors, *viz.*, hydration of kations (decrease of the effective mole-fraction or activity of water) and depolymerisation by anions (increase of the effective mole-fraction or activity of water), may be applied to determine the effective mole-fraction of water and thus the corrected van 't Hoff factor, i.

Washburn (*Tech. Quart.*, 1908, **21**, 373) has shown that the effective mole-fraction, n', of the solute may be calculated from the freezing-point depression, $\Delta t°$, by means of the equation

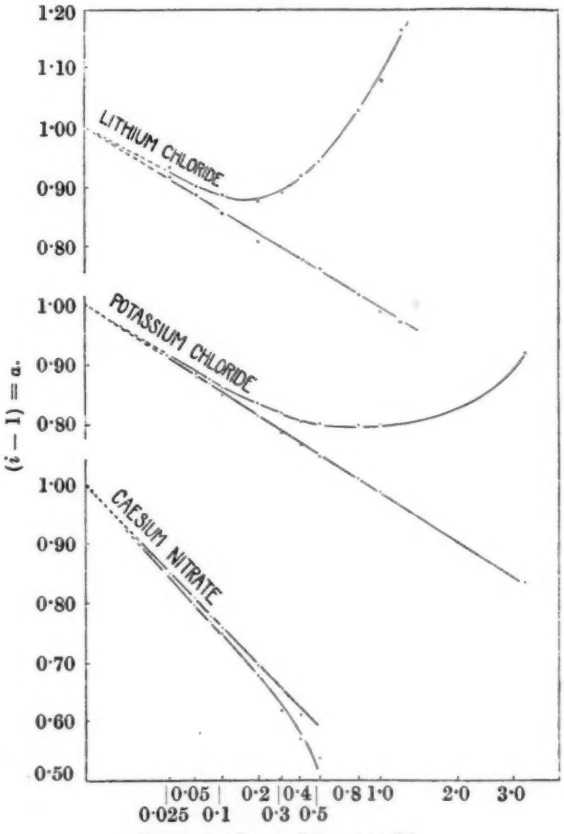
$$n' = 0{\cdot}00969\ (\Delta t - 0{\cdot}00425\Delta t^2) \quad . \quad . \quad . \quad . \quad (8)$$

This equation may be used for freezing-point depressions as large as 7°, and the mole-fraction is given with an accuracy equivalent to an experimental error of 0·001° in measuring Δt. Equation (8) may be equated to (*a*) $ni/(ni + N)$ and (*b*) $ni_c/(ni_c + N - Hn)$, where n and N are the numbers of gram-molecules of solute and solvent, and i and i_c the uncorrected and corrected van 't Hoff factor, respectively.

van 't Hoff's factor is defined on the basis of the classical theory by the equation (for a uni-univalent salt) $i = 1 + \alpha$, where α is the "degree of dissociation." Alternatively, $(1 - \alpha)$ may be regarded simply as the "osmotic deficiency," *i.e.*, the fraction by which the osmotic properties deviate from those required for an ideal solution of a completely dissociated salt. It was necessary, therefore, to review the recorded freezing-point depressions, more especially those referring to concentrated solutions where the hydration correction is considerable. Probably the most trustworthy measurements are those of Washburn and MacInnes (*loc. cit.*), who selected lithium chloride, potassium chloride, and cæsium nitrate as being representative of the whole range of hydrated salts, lithium chloride being presumably the most and cæsium nitrate the least heavily hydrated of the uni-univalent strong

electrolytes. In addition, the results of Noyes and Falk (*J. Amer. Chem. Soc.*, 1910, **32**, 1011), Jones and Pearce (*Amer. Chem. J.*, 1907, **38**, 683), Ponsot (*Ann. Chim. Phys.*, 1897, **10**, 79), de Coppet (*J. Physical Chem.*, 1904, **8**, 531; *Z. physikal. Chem.*, 1897, **22**, 239), Biltz (*Z. physikal. Chem.*, 1902, **40**, 185), Jahn (*ibid.*, 1904, **50**, 129; 1907, **59**, 31), Adams (*J. Amer. Chem. Soc.*, 1915, **37**,

FIG. 4.



Concentration (cube root scale).

481), Harkins and Hall (*ibid.*, 1916, **38**, 2658), Rodebush (*ibid.*, 1918, **40**, 1204), and Rivett (*Z. physikal. Chem.*, 1912, **80**, 546) have been used for the calculations, of which a selection is given in Table XI. In applying the hydration correction it was assumed that the hydration is (*a*) independent of the concentration and (*b*) has the same value at the freezing point as at 25°, the temperature at which the hydration determinations were made.

Table XI refers to lithium chloride, potassium chloride, and cæsium nitrate. In these three cases the corrected van 't Hoff factor, i_c, obeyed the dilution law

$$2 - i_c = K\sqrt[3]{n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

or

$$(1 - \alpha_c) = K\sqrt[3]{n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

with great accuracy, that is, the corrected "osmotic deficiency" $(1 - \alpha_c)$ is proportional to the cube root of the concentration or inversely proportional to the linear distance between the ions. The calculations were extended for potassium chloride to the cryohydric concentration, *i.e.*, 3·3 gram-molecules of salt per 1000 grams of solvent,* at which concentration the hydration correction † amounts to 20·2% of the total solvent present, an amount approximately the same as for molar lithium chloride solution. The figures for cæsium nitrate apply also to the cryohydric point of a 0·5 molar solution. The hydration of cæsium nitrate was obtained from Washburn's transport measurements (*J. Amer. Chem. Soc.*, 1915, **37**, 694) and the known value for potassium nitrate. Fig. 4 shows in a striking way the effect of the corrections, the straight lines representing the corrected and the curves the uncorrected values of α, plotted against the cube root of the concentration.

These results, obtained for three salts of the uni-univalent type, covering a wide hydration range appear to establish the cube root law as being the "dilution law" for strong electrolytes. The experimental difficulties in working with solutions more dilute than the above are very great. Moreover, a small error in Δt corresponds with a large error in $(1 - \alpha)$ and consequently in K, whilst the use of a constant value for H may not be justified in those dilute regions where the small change in curvature in the viscosity–concentration curve has been detected. It is, therefore, a difficult matter to test the applicability of the cube root law (applied to corrected values of α) to very dilute solutions. The curves in Fig. 4 differ, however, from the somewhat similar curves obtained by plotting the equivalent conductivity against the cube root of the concentration in this important respect, that whereas the extension of the latter to zero concentration involves an extrapolation to an unknown destination, λ_∞, the gap in these new curves may be bridged by a *linear interpolation*, since $(1 - \alpha)$ must be zero at zero concentration. Hence it appears probable that the cube root law may still be valid in this region; altern-

* This involves the use of Washburn's equation to a f. p. depression of 11°, but the small error thus introduced is probably not greater than the uncertainty with which the cryohydric temperature is known.

† Stated in the tables under the heading "%."

TABLE XI.

n.	Δt.	a.	a (corr.).	K.	a (calc.).	%.
		LiCl. $H = 10{\cdot}5$. $K = 0{\cdot}31$.				
0·025	0·090°	0·939	0·9295	0·241	0·910	0·48
0·050	0·177	0·9075	0·889	0·300	0·8865	0·94
0·075	0·265	0·905	0·880	0·285	0·873	1·44
0·1	0·351	0·8925	0·857	0·308	0·857	1·91
0·2	0·694	0·875	0·804	0·335	0·820	3·82
0·3	1·049	0·893	0·781	0·327	0·794	5·73
0·4	1·416	0·924	0·778	0·301	0·773	7·65
0·5	1·791	0·947	0·763	0·303	0·756	9·55
0·8	2·966	1·031	0·721	0·302	0·714	15·3
1·0	3·792	1·083	0·690	0·310	0·690	19·1
		KCl. $H = 3{\cdot}4$. $K = 0{\cdot}32$.				
0·025	0·089	0·917	0·914	0·294	0·907	0·15
0·050	0·175	0·886	0·880	0·326	0·883	0·31
0·075	0·262	0·878	0·870	0·309	0·869	0·46
0·1	0·345	0·8605	0·849	0·325	0·852	0·62
0·2	0·680	0·837	0·814	0·318	0·814	1·24
0·3	1·009	0·820	0·787	0·318	0·787	1·86
0·4	1·335	0·805	0·765	0·317	0·766	2·48
0·5	1·658	0·802	0·746	0·325	0·747	3·10
0·8	2·635	0·798	0·710	0·313	0·705	4·92
1·0	3·287	0·801	0·691	0·309	0·680	6·20
1·989	6·46	0·791	0·583	0·331	0·600	11·8 †
3·30 *	11·10	0·922	0·535	0·312	0·527	20·2 ‡
		$CsNO_3$. $H = 3{\cdot}3$. $K = 0{\cdot}52$.				
0·025	0·086	0·833	0·851	0·510	0·848	−0·15
0·05	0·168	0·807	0·812	0·510	0·809	−0·30
0·075	0·247	0·774	0·783	0·514	0·781	−0·45
0·1	0·352	0·753	0·763	0·511	0·759	−0·60
0·2	0·622	0·680	0·700	0·513	0·696	−1·2
0·3	0·897	0·618	0·647	0·527	0·652	−1·8
0·4	1·160	0·571	0·608	0·532	0·617	−2·4
0·5 *	1·419	0·539	0·585	0·531	0·588	−3·0

Washburn's values, except where marked † (Kistiakowski) and ‡ (de Coppet).

* Cryohydric concentration.

atively, if any departure from the law is involved, not one but two changes in curvature would be necessary in order that the osmotic deficiency should not have a finite value at infinite dilution.

The freezing-point measurements of Adams (*loc. cit.*) and Hovorka and Rodebush (*J. Amer. Chem. Soc.*, 1925, **47**, 1614) apply to dilute solutions, and are of a high order of accuracy, the former having been used to establish the freezing-point laws of Lewis and Linhart and of Brønsted. In Table XII their values of α_c are compared with the calculated values: s = g.-mol. of salt in 1000 g. of water.

The figures for potassium chloride agree (within the limits of experimental error) with one another and with the calculated values, but those for the nitrates show considerable divergences

Table XII.

s.	0·001	0·002	0·005	0·01	0·02	0·05	0·1
$(1-a) = 0{\cdot}32\sqrt[3]{n}$.	0·968	0·960	0·945	0·931	0·914	0·883	0·852
KCl. Adams.	—	0·969	0·961	0·942	0·920	0·883	0·851
„ H. & R.	0·962	—	0·956	0·933	—	—	—
„ W.	—	—	—	—	—	0·880	0·849
KNO_3. Adams.	—	0·967	0·958	0·938	0·910	0·853	0·797
$CsNO_3$. H. & R.	0·966	—	0·950	0·934	—	—	—
„ W.	—	—	—	—	—	0·812	0·763
$(1-a) = 0{\cdot}52\sqrt[3]{n}$.	0·948	0·934	0·911	0·888	0·859	0·808	0·759

Table XIII.

NaCl. $H = 7{\cdot}85$. $K = 0{\cdot}32$.

n.	Δt.	a.	a (corr.).	K.	a (calc.).	%.
0·005	0·01815°	0·953	0·952	0·281	0·945	0·07
0·01	0·036	0·938	0·936	0·297	0·931	0·14
0·02	0·0714	0·921	0·916	0·310	0·912	0·28
0·05	0·176	0·894	0·881	0·323	0·881	0·71
0·10	0·348	0·876	0·850	0·323	0·850	1·42
0·1168	0·406	0·875	0·8435	0·320	0·8435	1·66
0·235	0·808	0·859	0·797	0·329	0·802	3·32*
0·434	1·449	0·856	0·7445	0·340	0·760	6·0*
0·6148	2·068	0·831	0·6715	0·374	0·728	8·4†
0·9291	3·145	0·853	0·609	0·400	0·688	13·1†
			NH_4Cl. $H = 3{\cdot}3$. $K = 0{\cdot}32$.			
0·005	0·01818	0·947	0·946	0·316	0·941	0·04
0·01	0·036	0·928	0·927	0·339	0·931	0·06
0·02	0·071	0·908	0·906	0·346	0·912	0·12
0·05	0·1744	0·880	0·874	0·342	0·881	0·30
0·1	0·344	0·856	0·845	0·334	0·850	0·60
0·2	0·6784	0·832	0·811	0·323	0·813	1·2
0·2619	0·889	0·835	0·801	0·313	0·795	1·55*
0·3	1·0086	0·819	0·783	0·324	0·786	1·8
0·7974	2·658	0·820	0·734	0·287	0·703	4·75*
1·0523	3·51	0·830	0·715	0·283	0·675	6·3*
2·32	7·72	0·863	0·611	0·294	0·576	13·9‡
3·727	12·52	0·934	0·506	0·319	0·504	22·1‡
			RbCl. $H = 2{\cdot}9$. $K = 0{\cdot}32$.			
0·1095	0·379	0·867	0·856	0·301	0·845	0·58*
0·2404	0·812	0·826	0·800	0·322	0·799	1·27*
0·4061	1·347	0·7985	0·7605	0·323	0·762	2·12*
0·5866	1·927	0·788	0·732	0·320	0·730	3·06*
0·7608	2·483	0·792	0·721	0·306	0·705	4·0*
			CsCl. $H = 2{\cdot}7$. $K = 0{\cdot}32$.			
0·02	0·0717	0·931	0·929	0·262	0·912	0·1
0·05	0·1757	0·893	0·889	0·301	0·881	0·25
0·1	0·3454	0·863	0·854	0·315	0·850	0·50
0·2	0·677	0·8285	0·810	0·325	0·811	1·0
0·3	1·002	0·808	0·780	0·327	0·784	1·5
0·4	1·322	0·792	0·755	0·332	0·762	2·0
0·5	1·637	0·778	0·734	0·340	0·744	2·5
0·693	2·24	0·761	0·6995	0·340	0·714	3·5*

Noyes and Falk's values, except those marked * (Biltz), † (Ponsot), and ‡ (Rodebush).

(compare KNO_3 Adams with $CsNO_3$ Washburn) and in the most dilute solutions agree better with the calculated value for chlorides ($K = 0{\cdot}32$) than for nitrates ($K = 0{\cdot}52$).

Table XIII refers to the four remaining univalent chlorides. With the exception of sodium chloride, they all obey the law in a satisfactory way, having a common value of $K = 0{\cdot}32$. Sodium chloride deviates somewhat, the value of K increasing with concentration for solutions above $0{\cdot}25N$. This is unexpected, since the viscosity is normal, and lithium chloride with its greater hydration number obeys the law, as does sodium bromide (Table XIV).

Table XIV gives a representative selection of the other salts investigated, *viz.*, sodium bromide, magnesium chloride, barium chloride, and strontium nitrate, and it will be seen that in each

TABLE XIV.

n.	Δt.	a.	a (corr.)	K.	a (calc.)	%.
		NaBr. $H = 6{\cdot}4$. $K = 0{\cdot}29$.				
0·02	0·0722°	0·944	0·944	0·203	0·923	0·23†
0·05	0·1775	0·910	0·903	0·263	0·895	0·56†
0·1	0·3507	0·891	0·867	0·286	0·868	1·1†
0·2	0·6926	0·871	0·829	0·292	0·833	2·2†
0·3	1·031	0·860	0·798	0·301	0·809	3·4†
0·4872	1·691	0·886	0·783	0·276	0·772	5·4‡
0·6434	2·232	0·890	0·755	0·284	0·750	7·2‡
0·9731	3·413	0·923	0·707	0·296	0·713	10·9‡
1·1632	4·112	0·946	0·694	0·291	0·695	13·0‡
1·3544	4·820	0·965	0·670	0·291	0·671	15·1‡
		$MgCl_2$. $H = 24{\cdot}8$. $K = 0{\cdot}49$.				
0·0562	0·282	0·852	0·818	0·475	0·812	2·60‡
0·1180	0·580	0·827	0·757	0·495	0·760	5·3‡
0·1665	0·822	0·834	0·735	0·482	0·730	7·45‡
0·25072	1·235	0·835	0·682	0·504	0·691	11·5
0·5046	2·6768	0·999	0·622	0·475	0·610	22·5
0·76106	4·433	1·09	0·552	0·491	0·553	34·0
0·9608	6·062	1·34	0·503	0·504	0·517	43·0
		$BaCl_2$. $H = 16{\cdot}2$. $K = 0{\cdot}55$.				
0·05005	0·2477	0·833	0·817	0·497	0·797	1·46
0·07514	0·3613	0·796	0·762	0·564	0·768	2·2
0·1003	0·4792	0·789	0·751	0·536	0·745	2·8
0·16312	0·757	0·754	0·695	0·558	0·699	4·75§
0·1727	0·804	0·758	0·694	0·550	0·694	5·05§
0·4043	1·902	0·779	0·628	0·502	0·593	11·8
1·205*	7·85	1·33	0·443	0·524	0·415	35·5‖
		$Sr(NO_3)_2$. $H = 6{\cdot}8$. $K = 0{\cdot}58$.				
0·1004	0·4587	0·733	0·718	0·607	0·730	1·2
0·2528	1·0817	0·655	0·620	0·601	0·634	3·1
0·5116	2·0849	0·609	0·541	0·574	0·537	6·15
0·7771	3·0453	0·574	0·472	0·570	0·467	9·4
1·0506	3·9983	0·544	0·411	0·579	0·411	12·7
1·530*	5·75	0·543	0·352	0·562	0·332	18·4‖

Jones's values, except those marked † (Noyes and Falk), ‡ (Rivett), § (Ponsot), and ‖ (de Coppet).

* Cryohydric concentration.

case the cube root law is obeyed and applies equally well to bi-univalent salts of the type $BaCl_2$, $Sr(NO_3)_2$, etc.

In addition to the above salts, calculations have been made for a number of others with the following results: sodium nitrate ($K = 0{\cdot}38$), potassium nitrate ($K = 0{\cdot}50$), and rubidium nitrate ($K = 0{\cdot}51$) obey the cube root law, with the possible deviation of potassium nitrate in dilute solution (see Table XII and comments). The small value of K for sodium nitrate should be noted. Potassium bromide gave less satisfactory results, K decreasing from 0·31 for dilute solutions to 0·24 at the eutectic (3·836-weight normal). This salt behaves as if the hydration value of 1·9 is too small; the experimental result, however, is beyond suspicion. An increase of H by one unit (which is not justified on any other grounds) would give a constant value of K at all concentrations.

Calcium chloride ($K = 0{\cdot}47$), strontium chloride ($K = 0{\cdot}48$), cobalt chloride ($K = 0{\cdot}45$), and copper chloride ($K = 0{\cdot}52$) are all satisfactory. With barium nitrate ($K = 0{\cdot}80$), the constant tends to rise slightly, and with lead nitrate ($K = 0{\cdot}93$) to fall slightly, both in dilute solution; but this is thought to be due to possible small errors in the freezing-point measurements. Copper bromide gives a small but constant value ($K = 0{\cdot}31$), whilst barium bromide resembles the potassium salt, the values of K decreasing from 0·44 to 0·36.

Thus far, the results for twenty-two salts have either been given in detail or commented upon, and considerable evidence has been adduced in favour of the cube root law. In only three of the above cases do deviations occur, *viz.*, sodium chloride and potassium and barium bromides, but five other salts were found not to obey the law. These are the nitrates of lithium, magnesium, calcium, copper, and cobalt, for which K decreases continuously with increasing concentration: *e.g.*, magnesium nitrate $n = 0{\cdot}05$, $K = 0{\cdot}46$; $n = 1{\cdot}0423$, $K = 0{\cdot}13$; calcium nitrate $n = 0{\cdot}05$, $K = 0{\cdot}58$; $n = 1{\cdot}05$, $K = 0{\cdot}42$; lithium nitrate $n = 0{\cdot}04$, $K = 0{\cdot}52$; $n = 1{\cdot}016$, $K = 0{\cdot}24$. These salts all contain heavily hydrated kations, and anions which are very active in dissociating the solvent. Although the hydration numbers of these salts are relatively small, since they represent the *difference* between two competing processes, they do not afford a measure of the great disturbance suffered in these cases by the solution.

The apparent molecular hydration of magnesium nitrate is 12·8 H_2O; in a molar solution of this salt, not less than half the solvent is attached to the magnesium ions and the activity of the remainder is increased by 50% by the nitrate ions. It is doubtful, therefore, whether the use of a *constant* hydration correction is

permissible, even if Washburn's equation is applicable to cases where the solvent equilibrium is so violently disturbed. Where the absolute hydration correction is small (potassium chloride) the cube root law is followed with great exactness, even for dilute solutions, and it appears probable that an ideal strong electrolyte (anion inert, kation not hydrated) would obey the law over the whole concentration range.

The Hydration Theory and the Conductivity Ratio.

According to the theory of complete dissociation, the conductivity ratio λ_v/λ_∞ must be regarded solely as a ratio of mobilities, the mobility of the ions decreasing as the concentration increases, and this decrease is probably to a large degree due to the decreasing distance between the charged ions. If no other influence intervened, it is to be expected that the conductivity ratio would depend only on the type of salt and be independent of the ion carrying the charge. We know, however, that the so-called "dissociating power" of a solvent depends on the magnitude of its dielectric constant, whilst the latter is related to the molecular association of the solvent. The hydration theory suggested in this paper postulates a continuous decrease in the association of the solvent, and consequently a decrease in the dielectric constant, with increasing salt concentration, whilst the efficiency of the depolymerisation process varies with different anions. The conductivity ratio, therefore, should not only decrease as the concentration of salt increases, but it should do so at rates which depend on the sequence of the hydration numbers (see p. 186). For the potassium salts at semi-normal concentration at 18°, the order of the conductivity ratios is that required by the hypothesis, *viz.*, KCl, 0·779; KBr, 0·766; $KClO_3$, 0·703; KNO_3, 0·688.

Experimental.

The amyl alcohol was washed with dilute sulphuric acid and with water, dried over potassium carbonate, and distilled, the fraction boiling at 128—132° being collected. The distribution coefficients were determined by shaking together 100 c.c. of the alcohol, 100 c.c. of the solution to be examined, and 1 c.c. of purified acetic acid at 25° until equilibrium was established. After the two phases had separated completely, the alcoholic layer was drawn off rapidly and the acid content determined by titration with $N/20$-barium hydroxide and phenolphthalein. Owing to the different nature of the two solvents it was found advisable to wash out the pipette with either 20 c.c. of water or 20 c.c. of purified ethyl alcohol, according as the aqueous or non-aqueous

phase was being examined. In the latter case, the ethyl alcohol brought the amyl alcohol into complete solution and so facilitated the titration. It was necessary to carry out blank experiments on each batch of amyl alcohol, owing to slight variations of the coefficient with different samples (presumably due to differences in the proportion of the isomerides present). The average value of the coefficient alcohol to water was 0·96.

The viscosity measurements were carried out in an Ostwald viscosimeter at 20°, and whilst no outstanding accuracy is claimed for these results, all ordinary precautions were observed.

Summary.

The hydration of sucrose and some strong electrolytes has been determined from the distribution of acetic acid between their aqueous solutions and amyl alcohol. The results indicate that the hydration is (over the concentration range examined) independent of dilution and is an additive property which may have either a positive or a negative value.

A modified hydration theory is suggested according to which only kations are hydrated whilst anions depolymerise the solvent molecules. The first process tends to decrease and the second to increase the activity of the water. Hydration is therefore a composite effect, the salts having negative hydration numbers being those in which the influence of the anion predominates. Solutions of such salts have abnormally high vapour pressures.

The hydration theory has been correlated with viscosity phenomena and a semi-empirical equation established by means of which hydration values can be calculated from viscosity data.

A hydration correction has been applied to calculations of the "degree of dissociation" of strong electrolytes from freezing-point measurements, and evidence is adduced in favour of a cube root dilution law $(1 - \alpha) = K\sqrt[3]{n}$. Many salts have been shown to obey the law with great exactness, and those which do not do so are extreme cases in which the application of the correction is least certain.

Corroborative evidence for the new theory has been obtained from a consideration of the conductivity ratios of a number of strong electrolytes.

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XXIX.—*Action of Acetylene Tetrabromide on Organic Bases.*

By James Davidson Fulton.

The present investigation, in which the reagents were allowed to react in the absence of a solvent, was suggested by the action of nicotine on acetylene tetrabromide. The rotation of the solution changed rapidly from negative to positive and the solution became hot and coloured; after a few days a solid separated, whilst some oily matter remained. The latter, usually small in amount, was discarded in this and subsequent experiments.

The interaction of aniline and acetylene tetrabromide at the ordinary temperature was investigated by Sabanejev (*Annalen*, 1875, **178**, 125), who obtained a number of products including acetylenetriphenyltriamine, $C_{20}H_{17}N_3$. Schoop (*Ber.*, 1880, **13**, 2196) obtained octamethyltetra-aminotetraphenylethane by heating dimethylaniline with acetylene tetrabromide for 8 days. Elbs and Neumann (*J. pr. Chem.*, 1898, **58**, 250) failed to substantiate all the findings of Sabanejev. In the above cases, the hydrobromide of the base also was obtained. Dehn (*J. Amer. Chem. Soc.*, 1912, **34**, 286) has shown that the reaction of bases and acetylene tetrabromide in dry ether furnishes the hydrobromide and tribromoethylene quantitatively and that sunlight accelerates the reaction.

In the present instance, in the case of tertiary bases additive compounds of the hydrobromide with acetylene tetrabromide were obtained. The influence of sunlight on their formation was not marked. Abnormal bromoaurates were obtained from nicotine and quinoline.

Experimental.

Acetylene tetrabromide (usually 2 or 3 mols.) was added to the base (1 mol.) in the cold. Solid hydrobromides were immediately precipitated from primary and secondary amines. With tertiary bases, a solid separated after a day or two. In the case of α-picoline, although reaction was apparent, no crystals appeared for weeks until the mixture was cooled in liquid air and again left. The solid product was filtered off, freed from oily matter, and crystallised from alcohol. The well-crystallised substances thus obtained were all soluble in cold methyl or ethyl alcohol and very soluble in the hot solvent; repeated crystallisation brought about a partial change to the hydrobromide. A single crystallisation from acetone or chloroform effects this change almost completely. The compounds are slightly or not at all soluble in other common organic solvents. The total bromine and the ionisable bromine were estimated.

Water decomposes these compounds. Acetylene tetrabromide is liberated, and the supernatant aqueous solution contains the hydrobromide of the base, which was recognised, in the case of pyridine and quinoline, by analysis and melting point.

The bromoaurates separated when hot alcoholic solutions of the additive compounds, to which auric bromide in alcohol had been added, were allowed to cool.

Nicotine: $C_{10}H_{14}N_2,2HBr,2C_2H_2Br_4$, needles, or rhombs by slow crystallisation, m. p. 178—180° (decomp.), softening at 140° (Found: total Br, 79·0, Br′, 15·9. Calc., 78·7 and 15·7%, respectively). $[\alpha]^{17°}_{Hg\text{-}green}$ + 3·21° in alcohol (c = 5·6025).

The *bromoaurate*, $C_{10}H_{14}N_2,2HBr,AuBr_3$, forms dark red crystals, m. p. 183°, which are soluble in alcohol and slightly soluble in water (Found: Au, 26·05. Calc., Au, 25·9%).

A more stable, less soluble compound, $[\alpha]^{17°}_{Hg\text{-}green}$ + 6·96° in alcohol (c = 5·6025), m. p. 182—183° (decomp.), giving the same bromoaurate (Found: Au, 26·0%), was obtained by repeated crystallisation of the above and also from 1 mol. of the base and 1 mol. of acetylene tetrabromide [Found: total Br, 64·4; Br′, 32·3. $(C_{10}H_{14}N_2,2HBr)_2,C_2H_2Br_4$ requires Br, 64·4; Br′, 32·2%].

Pyridine: $C_5H_5N,HBr,C_2H_2Br_4$, colourless crystals, m. p. 108—109° (Found: total Br, 79·15; Br′, 16·05. Calc., Br, 79·05; Br′, 15·8%).

The *bromoaurate* forms brownish-red crystals, m. p. 318—319° (Found: Au, 33·0. $C_5H_5N,HBr,AuBr_3$ requires Au, 33·0%).

Quinoline: The product was washed with a little alcohol and ether. It softened at 115° and melted at 136° [Found: total Br, 62·4; Br′, 21·2. $(C_9H_7N,HBr)_2,C_2H_2Br_4$ requires Br, 62·7; Br′, 20·9%]. This substance is analogous to the lead compound, $(C_9H_7N,HBr)_2,PbBr_4$ (Classen and Zahorski, *Z. angew. Chem.*, 1891, **4**, 107).

The *bromoaurate* forms dark red crystals, m. p. 171—172°, which are soluble in alcohol and slightly soluble in water [Found: Au, 23·0. $(C_9H_7N,HBr)_2,AuBr_3$ requires Au, 23·0%]. It is analogous to Fenner and Tafel's chloro-compound (*Ber.*, 1899, **32**, 3227).

iso*Quinoline* gave mostly its hydrobromide, m. p. 207° (Found: Br, 38·0. Calc., Br, 38·1%). The additive compound, m. p. 155—156°, was almost colourless and not quite pure [Found: total Br, 61·4; Br′, 22·5. $(C_9H_7N,HBr)_2,C_2H_2Br_4$ requires Br, 62·7; Br′, 20·9%].

The bromoaurate, obtained from the hydrobromide in dark red crystals, m. p. 223°, was normal (Found: Au, 30·25. Calc. for $C_9H_7N,HBr,AuBr_3$, Au, 30·5%).

Lutidine, b. p. 153—156° (regarded as 2 : 4-dimethylpyridine):

Colourless crystals, m. p. 135—140° [Found : total Br, 66·7; Br′, 22·3. $(C_7H_9N,HBr)_2,C_2H_2Br_4$ requires Br, 66·5; Br′, 22·2%].

α-Picoline : $C_6H_7N,HBr,C_2H_2Br_4$, colourless needles, m. p. 104—105° (Found : total Br, 76·8; Br′, 15·4. Calc., Br, 76·9; Br′, 15·4%).

Interaction of acetylene tetrabromide and piperidine, coniine, homopiperonylamine, menthylamine, hexamethylenetetramine, and phenylhydrazine gave rise to the hydrobromide only. Antipyrine dissolved in hot acetylene tetrabromide crystallised unchanged on cooling. Pyrrole also did not react.

I desire to thank Professor T. S. Patterson for his interest in this work and for facilities to carry it out.

THE UNIVERSITY, GLASGOW. [*Received, October 2nd,* 1925.]

XXX.—*Heterogeneous Equilibria between the Sulphates and Nitrates of Sodium and Potassium and their Aqueous Solutions. Part I. The Ternary Systems.*

By MOHAMMED ABDUL HAMID.

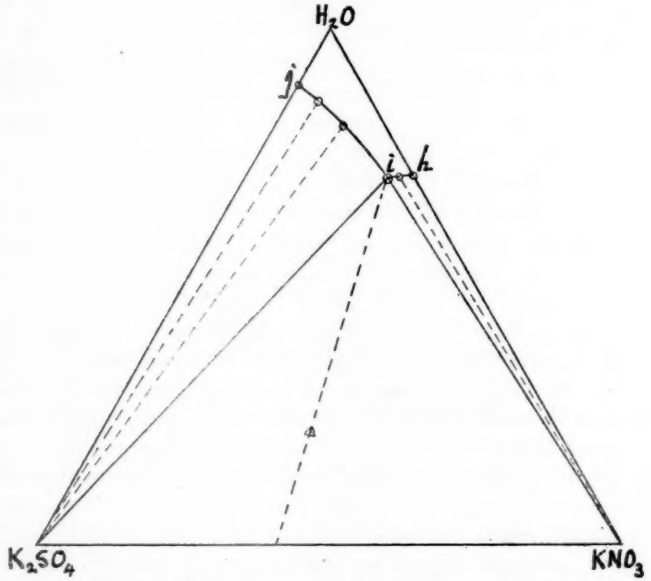
DURING the course of an investigation of the quaternary system H_2O–Na_2SO_4–$NaNO_3$–K_2SO_4–KNO_3 at 25° and 90°, it became necessary to investigate and revise some of the ternary systems involved. The subject of the present paper is to record the data so obtained and to sum up briefly all other information available about the isothermal relations in the four ternary systems which form the basis of the above quaternary system. In the isotherms at 90°, only the invariant points have been determined. The solubilities of single salts have been selected from Seidell's "Solubilities of Inorganic and Organic Substances." The vapour phase is always assumed to be absent and the whole subject is treated from the point of view of condensed systems at atmospheric pressure.

EXPERIMENTAL.

All the salts used were carefully purified by repeated crystallisation and their purity was checked by a number of analyses before use. For the determination of solubility, various complexes were vigorously stirred up to equilibrium in wide tubes immersed in water- and oil-thermostats kept constant within 0·02° at 25° and within 0·2° at 90°. The usual time given was about 40 hours at 25° and about 10 hours at 90°. The compositions of the solutions when equilibrium was established were determined by withdrawing

portions of them by means of pipettes heated previously to the temperatures of the baths, filtering, and weighing in stoppered bottles and analysing the solutions. The moist residue was weighed separately and analysed. The potassium ion was determined by the cobaltinitrite method, sulphate weighed as barium sulphate, and nitrate estimated by a modified method of Schlösing. All these methods were checked beforehand by a large number of estimations in mixtures of sodium sulphate, sodium nitrate, potassium sulphate, and potassium nitrate of known compositions. The amounts of sodium and water were determined by difference. In some cases all the salts were converted into the chlorides and the analytical results checked in this way.

FIG. 1.



The thermometers were all compared with those standardised at the National Physical Laboratory, Teddington.

The System Water–Potassium Sulphate–Potassium Nitrate.—This belongs to the simplest type of ternary system, neither double salts nor salt hydrates occurring in it. The system at 25° is represented graphically in Fig. 1, and the experimental data for the two temperatures are in Table I.

The system water–sodium nitrate–potassium nitrate has been worked out by Reinders (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1065) at 25°. The compositions of the binary and ternary invariant solutions at 90° are in Table II.

TABLE I.

Composition by weight percentage.

Temp.	Solution. % K_2SO_4.	Solution. % KNO_3.	Rest. % K_2SO_4.	Rest. % KNO_3.	Solid phases.
25°	10·74	0	—	—	K_2SO_4
,,	8·85	4·82	—	—	,,
,,	6·89	11·05	—	—	,,
,,	4·45	23·99	43·18	36·75	K_2SO_4 + KNO_3
,,	1·98	26·01	—	—	KNO_3
,,	0	27·97	—	—	,,
90°	18·57	0	—	—	K_2SO_4
,,	0·63	65·92	—	—	K_2SO_4 + KNO_3
,,	0	66·90	—	—	KNO_3

TABLE II.

Composition by weight percentage.

% $NaNO_3$.	% KNO_3.	Solid phases.
61·65	0	$NaNO_3$
37·57	45·26	$NaNO_3$ + KNO_3
0	66·90	KNO_3

The system water–potassium sulphate–sodium sulphate is complicated by the existence of a double sulphate of sodium and potassium known as the mineral glaserite. As to the composition of this compound, there have been controversies from time to time. Its correct composition was first reported by Penny (*Phil. Mag.*, 1855, **10**, 401), who assigned the formula $3K_2SO_4,Na_2SO_4$ to it and after whom it is sometimes called Penny's double salt. Penny's results were corroborated by some authors, whilst several double sulphates of sodium and potassium of different compositions were subsequently described by various investigators. A complete literature on this subject can be found in a paper by Retgers (*Z. physikal. Chem.*, 1890, **6**, 205). van 't Hoff and Barschall (*Berlin. Sitzungsber.*, 1903, 359; *Z. physikal. Chem.*, 1906, **56**, 212) put forward the view that glaserite is an extreme limit of a series of solid solutions saturated with potassium sulphate having the composition $K_3Na(SO_4)_2$. Nacken (*Berlin. Sitzungsber.*, 1910, 1016) has confirmed the existence of the double salt $K_3Na(SO_4)_2$ and has found that it dissolves sodium sulphate as a solid solution up to a certain extent. His results have been confirmed recently by Okada (*Mem. Coll. Sci.*, 1914, **1**, 95). Whereas Nacken assumes that the solubility of sodium sulphate in glaserite increases with temperature, Okada has shown that it increases to a temperature of 60°, where it reaches a maximum, and above that temperature the field of solid solutions becomes narrower again. The system H_2O–K_2SO_4–Na_2SO_4 at 25° and 90° is shown in Figs. 2 and 3

respectively. The data for this system at these two temperatures are in Table III.

TABLE III.

Composition by weight percentage.

Temp.	% Na_2SO_4.	% K_2SO_4.	Solid phases.
25°	21·84	0	$Na_2SO_4,10H_2O$
,,	19·93*	7·06	$Na_2SO_4,10H_2O$ + mixed crystals of $K_3Na(SO_4)_2$ and Na_2SO_4
,,	5·58*	11·27	$K_2SO_4 + K_3Na(SO_4)_2$
,,	0	10·74	K_2SO_4
90°	29·90	0	Na_2SO_4
,,	27·05	8·33	Na_2SO_4 + mixed crystals of Na_2SO_4 and $K_3Na(SO_4)_2$
,,	9·23	14·97	$K_2SO_4 + K_3Na(SO_4)_2$
,,	0	18·57	K_2SO_4

* Meyerhoffer and Saunders, *Z. physikal. Chem.*, 1899, **28**, 482.

FIG. 2.

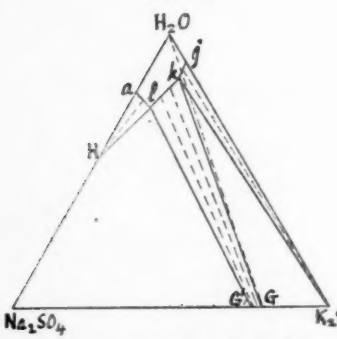
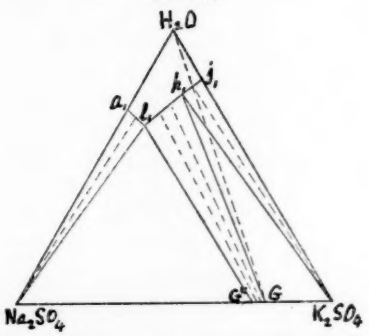


FIG. 3.



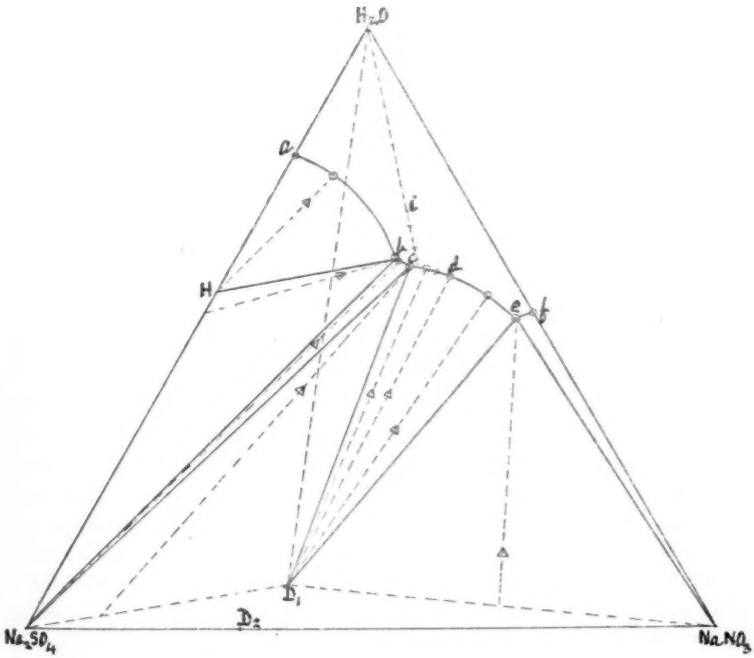
The points H and G (Figs. 2 and 3) represent the compositions of pure Glauber's salt and pure glaserite, respectively. The point G′ (Fig. 2) represents the composition of the solid solution containing the maximum amount of sodium sulphate which glaserite can dissolve at 25°. Similarly the point G″ (Fig. 3) represents the composition of the solid solution which is formed by dissolving the maximum amount of sodium sulphate in glaserite at 90°. The compositions of G, G′, and G″ are given in Table IV, both in terms of weight (w) and molar (m) percentages.

TABLE IV.

	Comp. of G.		Comp. of G′.		
Temp. 25° :	K_2SO_4.	Na_2SO_4.	K_2SO_4.	Na_2SO_4.	Diff.
m	75·0	25·0	71·7	28·3	3·3
w	78·6	21·4	75·7	24·3	2·9
	Comp. of G.		Comp. of G″.		
Temp. 90° :	K_2SO_4.	Na_2SO_4.	K_2SO_4.	Na_2SO_4.	Diff.
m	75·0	25·0	70·5	29·5	4·5
w	78·6	21·4	74·6	25·4	4·0

The above values of G′ are taken from Nacken and Okada and those of G″ interpolated from Okada's results. It will be seen from the isotherms at 25° and 90° (Figs. 2 and 3) that the solutions l and l_1 are in equilibrium with Glauber's salt and G′ in one case, and with sodium sulphate and G″ in the other. The solutions all along the curves lk and l_1k_1 are in equilibrium with solid solutions whose compositions vary between G and G′ in one case and between G and G″ in the other. It may be mentioned that glaserite is not known to form any solid solutions with potassium sulphate.

FIG. 4.



The System Water–Sodium Sulphate–Sodium Nitrate.—This system has been very recently worked out by Massink (*Z. physikal. Chem.*, 1917, **92**, 364) at a number of temperatures. In addition to a hydrated double salt of the formula $Na_2SO_4,NaNO_3,H_2O$, commonly known in Chile as the mineral darapskite, Massink describes an anhydrous double salt of the formula $3NaNO_3,4Na_2SO_4$ at 25°. No evidence of this double salt could be obtained at this temperature. The only double salt that exists at 25° is the hydrated double salt, darapskite, which breaks up at higher temperatures, and at 90° the only stable solid phases in the system are the two anhydrous

salts, sodium sulphate and sodium nitrate. The system at 25° is shown in Fig. 4, and the data for this system at the two temperatures are in Table V.

TABLE V.

Composition by weight percentage.

	Solution.		Rest.		
Temp.	% Na_2SO_4.	% $NaNO_3$.	% Na_2SO_4.	% $NaNO_3$.	Solid phases.
25°	21·84	0	—	—	$Na_2SO_4,10H_2O$
,,	17·52	7·48	23·37	6·15	,,
,,	15·70	23·43	24·82	16·58	$Na_2SO_4,10H_2O + Na_2SO$
,,	15·43	24·06	34·43	18·40	Na_2SO_4
,,	14·15	25·96	39·87	20·45	$Na_2SO_4 + D_1$
,,	11·88	28·46	30·00	31·05	D_1
,,	9·04	32·68	27·44	33·46	,,
,,	5·42	39·71	29·39	37·52	,,
,,	3·01	45·87	24·63	62·90	$D_1 + NaNO_3$
,,	0	47·69	—	—	$NaNO_3$
90°	29·90	0	—	—	Na_2SO_4
,,	2·53	58·66	—	—	$Na_2SO_4 + NaNO_3$
,,	61·65	0	—	—	$NaNO_3$

Composition of D_1 = Na_2SO_4, 57·96%; $NaNO_3$, 34·68%; H_2O, 7·36%.

The points H and D_1 (Fig. 4) represent the compositions of pure Glauber's salt and pure darapskite, respectively. The point D_2 (Fig. 4) represents the composition of the supposed anhydrous double salt of Massink and the point *d* his supposed ternary isothermal invariant point at which, according to him, the solution is in equilibrium with darapskite and the anhydrous double salt D_2. Not only has this solution been found to be saturated with darapskite alone, but on isothermal evaporation of unsaturated solutions at 25° which theoretically ought to have deposited the anhydrous double salt D_2, if it could exist, darapskite has been found to be precipitated as the first solid. Thus an unsaturated solution of the composition *i* (Fig. 4) on evaporation at 25°, according to Massink, should deposit the anhydrous double salt D_2 as the first solid and should continue to do so until the point *d* is reached. This it does not do. Instead, however, it deposits darapskite, which comes down in very fine, needle-shaped crystals, readily distinguishable with the naked eye. Besides the double salt D_2, Massink (*loc. cit.*) describes another anhydrous double salt of the formula $3NaNO_3,2Na_2SO_4$ at 35°. It may be noted that he has determined the compositions of these two anhydrous double salts from one or two analyses of the solution and the wet residue in each case, which in themselves are not sufficient. The improbability of the existence of these two anhydrous double salts in this system is further manifest from the following considerations. It has been

alleged by Massink himself that these two anhydrous double salts do not exist at lower temperatures. According to him, the transition temperatures which mark the lower stability limits to the existence of the two anhydrous double salts lie somewhere between 20° and 35°. Further, it has been shown by Schreinemakers (*Z. physikal. Chem.*, 1909, **65**, 553) that if two anhydrous salts can form an anhydrous double salt at a certain temperature in the binary system, formed by these two salts, they will do so at the same temperature in all ternary systems formed by the addition of any liquid component to the above binary system, and the solubility curves of the two salts will be interrupted by that of the double salt in all these systems at this temperature. The converse of this principle has been very recently applied by Freeth (*J. Physical Chem.*, 1925, **29**, 1497) in the deduction of the type of a two-component system by the addition of a third component, from which it follows that if above a certain temperature in the ternary system H_2O–Na_2SO_4–$NaNO_3$ the solubility curves of sodium sulphate and sodium nitrate are interrupted by that of an anhydrous double salt, this will be the case also in the binary system Na_2SO_4–$NaNO_3$. Since the solution does not participate in the formation of the anhydrous double salt, the transition temperature of this binary compound is independent of the number of components of the system, *i.e.*, it is the same in all systems whether binary, ternary, or quaternary. It is clear, therefore, that at temperatures above 35° the two anhydrous double salts of Massink, if they can exist at all, must be formed in the ternary system H_2O–Na_2SO_4–$NaNO_3$ as also in the binary system Na_2SO_4–$NaNO_3$. From an investigation of the quaternary system H_2O–Na_2SO_4–$NaNO_3$–K_2SO_4–KNO_3 at 90° the author has been led to the conclusion that no such double salts exist in the ternary system H_2O–Na_2SO_4–$NaNO_3$ at this temperature, the only solid phases being the two anhydrous salts, sodium sulphate and sodium nitrate. This is in complete accord with the very recent investigations of Perman and Harrison (J., 1924, **125**, 365) of the binary system Na_2SO_4–$NaNO_3$.

The author wishes to express his thanks to Professor F. G. Donnan, F.R.S., for his kind help and interest during the course of this investigation.

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XXXI.—*Heterogeneous Equilibria between the Sulphates and Nitrates of Sodium and Potassium and their Aqueous Solutions. Part II. The Quaternary System* H_2O–Na_2SO_4–$NaNO_3$–K_2SO_4–KNO_3.

By Mohammed Abdul Hamid.

Beyond the observations of some early investigators of the slow dissolution of potassium nitrate in saturated sodium sulphate solutions with the precipitation of sodium or potassium sulphate after a long time and of the ease with which sodium nitrate dissolves in solutions of potassium sulphate, no attempt seems ever to have been made to study the equilibria involved in the reciprocal salt transformation

$$Na_2SO_4 + 2KNO_3 \rightleftharpoons 2NaNO_3 + K_2SO_4.$$

The quaternary system formed by the addition of water to the two salt pairs, Na_2SO_4–KNO_3 and $NaNO_3$–K_2SO_4 presents certain features of interest and is of special importance in the determination of the most suitable conditions for the separation of the nitrates of sodium and potassium from the sulphates of these metals, with which they are found contaminated in nature in various parts of the world.*

The various binary and ternary systems which form the basis of the above quaternary system have been described in Part I (preceding paper). All the binary and ternary compounds which occur in the ternary systems occupy definite saturation surfaces in the quaternary system. In addition to these binary and ternary compounds at 25°, a compound occurs in the quaternary system, the composition of which it has not been found possible so far to determine. It occupies a definite saturation surface in the quaternary system, and further evidence on which the conclusion of its existence is based will be found in the following pages. The isotherm at 90° does not contain the saturation surface of this compound. There is therefore no doubt that it splits up at some temperature below 90° into its simple constituents.

Graphical Representation.—In order to represent graphically the experimental results, Schreinemakers's pyramidal method of representation (*Z. physikal. Chem.*, 1909, **69**, 557) has been used. Use has also been made of the various projection methods (*ibid.*, 1907,

* See "Report on a Programme of Investigation for the Chilean Nitrate Industry," 1921, by Professor F. G. Donnan; the Report of the Indian Industrial Commission, 1916–18, Appendix F; and a Report on the Manufacture and Composition of Indian Saltpetre by Hooper (Agricultural Ledger, No. 3, 1905).

TABLE I.

The System H_2O–Na_2SO_4–$NaNO_3$–K_2SO_4–KNO_3 *at* 25°.

Composition in molar percentages.

Point.	Na_2SO_4.	$Na_2(NO_3)_2$.	K_2SO_4.	$K_2(NO_3)_2$.	Solid phases.
a	3·42	—	—	—	$Na_2SO_4,10H_2O$
	2·85	1·02	—	—	,,
b	3·05	3·80	—	—	$Na_2SO_4,10H_2O + Na_2SO_4$
l	3·35	—	0·96	—	$Na_2SO_4,10H_2O + D_2$
m	2·89	2·75	0·74	—	$Na_2SO_4,10H_2O + Na_2SO_4 + D_2$
	3·01	3·92	—	—	Na_2SO_4
c	2·78	4·27	—	—	$Na_2SO_4 + D_1$
	2·76	4·44	0·67	—	,,
n	2·66	4·49	1·27	—	$Na_2SO_4 + D_1 + D_2$
	2·34	4·70	—	—	D_1
	1·82	5·51	—	—	,,
	1·15	7·04	—	—	,,
e	0·68	8·63	—	—	$D_1 + NaNO_3$
	0·74	8·47	—	0·23	,,
r	1·05	7·91	—	0·60	$D_1 + NaNO_3 + T$
f	—	8·81	—	—	$NaNO_3$
	—	8·97	—	0·40	,,
	—	9·03	—	0·80	,,
	—	9·10	—	1·59	,,
	—	9·18	—	2·36	,,
g	—	9·31	—	3·58	$NaNO_3 + KNO_3$
	1·17	8·36	—	1·69	$NaNO_3 + T$
	0·77	8·97	—	3·20	,,
s	0·67	9·10	—	3·63	$NaNO_3 + KNO_3 + T$
	—	5·78	—	3·39	KNO_3
	—	3·94	—	3·26	,,
	—	2·01	—	3·17	,,
	—	1·52	—	3·18	,,
	—	1·02	—	3·20	,,
	—	0·51	—	3·26	,,
h	—	—	—	3·34	,,
	—	—	0·28	3·11	,,
i	—	—	0·62	2·89	$KNO_3 + K_2SO_4$
	—	—	0·85	1·18	K_2SO_4
	—	—	1·04	0·49	,,
j	—	—	1·23	—	,,
k	0·83	—	1·34	—	$K_2SO_4 + D_2$
	1·18	—	1·09	0·44	,,
	1·09	—	0·89	0·69	,,
	0·99	—	0·32	1·75	,,
v	—	1·16	0·92	2·70	$K_2SO_4 + D_2 + KNO_3$
	—	2·12	0·99	2·32	$D_2 + KNO_3$
	—	4·91	1·33	1·82	,,
q	—	7·91	1·61	1·65	$D_2 + KNO_3 + T$
	—	8·47	0·96	2·32	$KNO_3 + T$
	1·63	5·42	1·60	—	$D_1 + D_2$
	1·08	6·35	1·92	—	,,
	0·75	7·13	2·09	—	,,
	0·13	8·32	2·30	—	,,
p	—	9·13	2·27	0·41	$D_1 + D_2 + T$
	—	8·82	1·90	0·84	$D_2 + T$

$D_1 = Na_2SO_4,NaNO_3,H_2O$. $D_2 = K_3Na(SO_4)_2$. T = ?.

59, 663) for the confirmation of solid phases by the " rest method " in certain parts of the system. It may be pointed out that by the term, orthogonal projection, is meant a projection made on to the

ground plane by means of parallel lines perpendicular to the base of the pyramid.

The experimental and analytical methods used were the same as described in Part I. The data for the system H_2O–$NaNO_3$–KNO_3 at 25° are taken from Reinders (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 106).

The Isotherm at 25°.—The compositions of the binary, ternary and quaternary solutions saturated at this temperature are expressed in g.-mols. of the various salts per 100 g. of the solution in Table I. The molecular formulæ of sodium and potassium nitrates have been doubled in order to give them equal replacing powers with sodium and potassium sulphates.

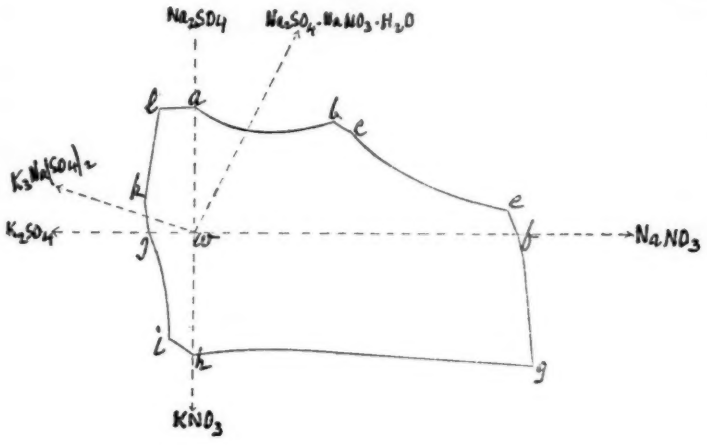
The Orthogonal Projection.—For the further discussion of the system, we shall use the orthogonal projection which is shown in Figs. 1 and 2. The apex, W, of the pyramid which represents pure water projects to the point *w* in these figures. The four ternary isotherms which form the boundary of the quaternary isotherm are shown in this projection separately in Fig. 1. As has been pointed out in Part I, the point *l* represents a ternary isothermal invariant solution which is in equilibrium not with Glauber's salt and glaserite, but with Glauber's salt and a solid solution of glaserite and sodium sulphate of the composition $K_2SO_4 = 78{\cdot}6\%$, $Na_2SO_4 = 21{\cdot}4\%$. This introduces no new complication in the quaternary system provided there is always an excess of sodium sulphate present in the solid phase to form the solid solution of glaserite and sodium sulphate of the above composition. Strictly speaking, therefore, where glaserite is mentioned as a solid phase along with sodium sulphate, its composition is given by the above value. The difference between the composition of glaserite and that of its solid solution is not, however, very large and for all practical purposes glaserite may be assumed to be of the constant composition $K_3Na(SO_4)_2$. It may be seen that the line joining the point representing the composition of pure glaserite to the origin (apex in the space model) cuts the saturation curve of potassium sulphate and not that of glaserite. Glaserite is therefore decomposed by water and the ternary invariant solution *l* is incongruently saturated.

In order to show the positions of the quaternary saturation surfaces of Glauber's salt and sodium sulphate and the quaternary isothermal invariant point *m* more clearly in the projection, the ternary saturation curve *ab* of Glauber's salt in the system H_2O–Na_2SO_4–$NaNO_3$ is drawn as a straight line in Fig. 2, although the actual form of the curve is that shown in Fig. 1.

The darapskite field is enclosed by the curves *ce*, *er*, *rp*, *pn*, and *cn*. Here again the line joining the point representing the com-

position of pure darapskite to the origin passes through the Glauber's salt and glaserite fields and not through that of darapskite. Darapskite also is therefore decomposed by water.

FIG. 1.



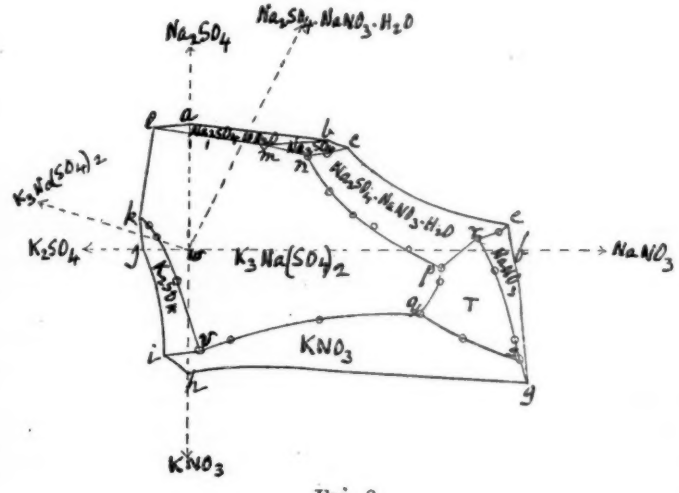


FIG. 2.

The quaternary saturation curves *er*, *rs*, and *sg* mark the inner boundary limit of the sodium nitrate field. The composition of the solution containing the maximum amount of potassium nitrate, which the ternary invariant solution *e* in contact with darapskite

and sodium nitrate can dissolve, is given by the point *s*. The same quaternary solution *s* is obtained when an excess of either sodium or potassium sulphate is added to the ternary invariant solution *g* in contact with excess of solid sodium and potassium nitrates.

The point *v* (Fig. 2) represents a quaternary invariant solution in equilibrium with three solid phases, potassium sulphate, glaserite and potassium nitrate. The composition of this solution, as will be seen from the position of the point *v* in Fig. 2, cannot be represented in terms of the solid phases with which it is in equilibrium. This solution is therefore incongruently saturated.

On the addition of sodium nitrate to the solution *v* in contact with glaserite, potassium sulphate and potassium nitrate, the following reaction occurs :

$$NaNO_3 + 2K_2SO_4 = K_3Na(SO_4)_2 + KNO_3.$$

This reaction does not affect the composition of the quaternary invariant solution *v*, so long as there is any solid potassium sulphate present in contact with the solution. When so much of the sodium nitrate has been added that the whole of the solid potassium sulphate which was present in contact with the solution *v* is converted into glaserite and potassium nitrate, it disappears as a solid phase and the system acquires a degree of freedom. The point representing the compositions of the monovariant quaternary solutions then traverses the curve *vq* on the additions of increasing quantities of sodium nitrate to the solution *v*. The two solid phases in equilibrium with all quaternary solutions, the compositions of which are represented by points on the curve *vq* between the points *v* and *q*, are glaserite and potassium nitrate. When so much of the sodium nitrate has been added that the composition of the quaternary solution is represented by the point *q*, a distinct halt occurs in the movement of the point representing the compositions of the quaternary solutions, and further additions of sodium nitrate do not change the composition of the solution *q*, so long as there is sufficient glaserite present in contact with it. It is the persistence of the constant composition of the solution at *q* in contact with solid glaserite and potassium nitrate with increasingly small additions of sodium nitrate that leaves no doubt as to *q* being an invariant point.

The above facts combined with the positions of the curves *np* and *pq* all point to the existence of a new solid phase in the quaternary system. Before describing the various attempts that have been made to determine the nature of this new solid phase, we shall sum up briefly the meanings of the various curves and surfaces in the

quaternary isotherm at 25°. The letter T stands for the new solid phase.

almb	is the	saturation	field of	Glauber's salt.
bcnm	,,	,,	,,	sodium sulphate.
cnpre	,,	,,	,,	darapskite.
efgsr	,,	,,	,,	sodium nitrate.
rpqs	,,	,,	,,	T
gsqvih	,,	,,	,,	potassium nitrate.
kjiv	,,	,,	,,	potassium sulphate.
klmnpqv	,,	,,	,,	glaserite and solid solutions of glaserite and sodium sulphate.

Quaternary curves :

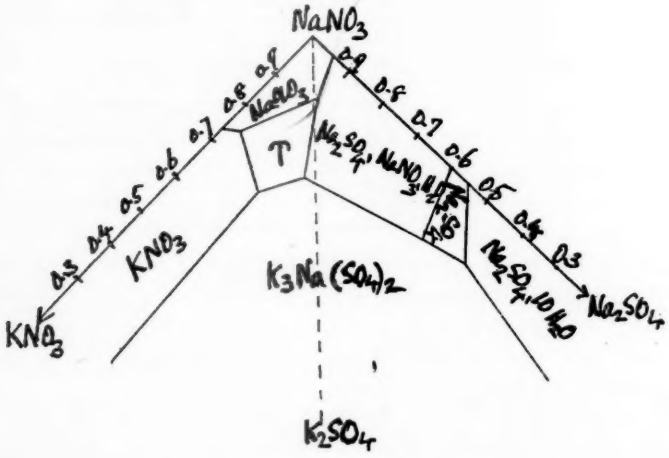
bm	is the	saturation	curve of	Glauber's salt and sodium sulphate.
lm	,,	,,	,,	Glauber's salt and glaserite.
mn	,,	,,	,,	sodium sulphate and glaserite.
cn	,,	,,	,,	sodium sulphate and darapskite.
np	,,	,,	,,	darapskite and glaserite.
er	,,	,,	,,	darapskite and sodium nitrate.
rp	,,	,,	,,	darapskite and the compound T.
rs	,,	,,	,,	sodium nitrate and the compound T.
gs	,,	,,	,,	sodium nitrate and potassium nitrate.
sq	,,	,,	,,	potassium nitrate and the compound T.
pq	,,	,,	,,	glaserite and the compound T.
qv	,,	,,	,,	glaserite and potassium nitrate.
iv	,,	,,	,,	potassium sulphate and potassium nitrate.
kv	,,	,,	,,	potassium sulphate and glaserite.

The saturation curves and surfaces intersect in points representing solutions which are saturated with three solids. These quaternary invariant points are *m*, *n*, *p*, *q*, *r*, *s*, and *v*. The actual compositions of these solutions as well as the solids with which they are in equilibrium will be found in Table I.

The Nature of the Phase T.—The improbability of the existence of any compound other than darapskite of sodium sulphate and sodium nitrate has been pointed out in Part I. The positions of the various quaternary invariant points and those of the quaternary saturation curves and the existence of the enclosed area *rpqs* in Fig. 2 point clearly to the formation of a definite compound in the quaternary system. That this is essentially a quaternary compound, a triple or a tetragenic double salt, is indisputable. Attempts to isolate it by the evaporation of unsaturated solutions have proved fruitless. It will be seen by reference to Fig. 2 that points in the area *rpqs* represent solutions which are saturated with one solid only, *viz.*, the compound T. The points representing the compositions of unsaturated solutions which will deposit this compound on isothermal evaporation as the first solid also project on to this area in the orthogonal projection. The compositions of all such unsaturated solutions which will deposit T as the first solid on evaporation cannot be read directly from this projection. Jänecke's method of representation (" Gessättigte Salzlösungen ") is of inestimable value

for this purpose. A part of the Jänecke diagram is shown in Fig. 3. The proportions of dry salts contained by an unsaturated solution which will deposit T as the first solid on evaporation can be read from this figure at a glance. To hasten the process of evaporation, such mixtures of dry salts were dissolved in excess of water and the unsaturated solutions evaporated at higher temperatures to such an extent that when cooled to 25° they were expected to deposit T as the first solid. This method of procedure unfortunately suffers from the serious defect that the solubility of sodium sulphate in solutions of potassium and sodium nitrates decreases with rise of temperature and consequently sodium sulphate is deposited at

FIG. 3.

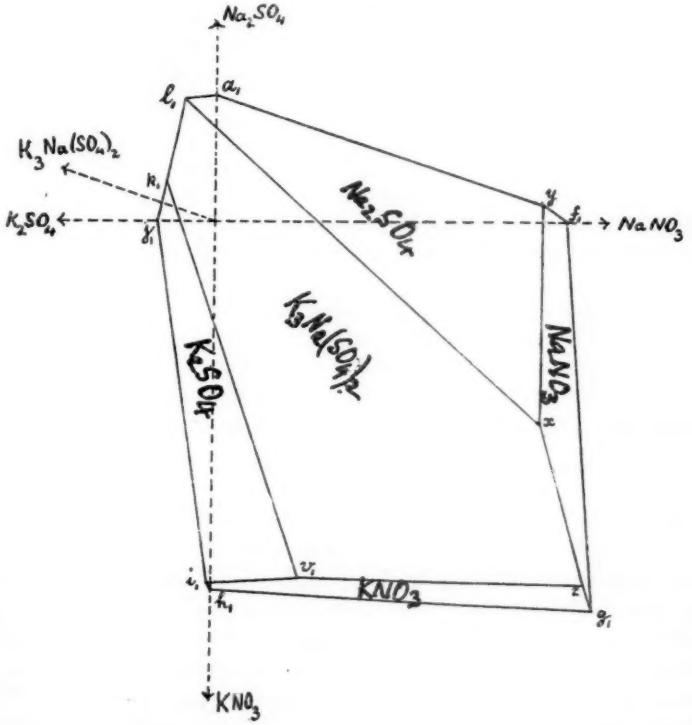


higher temperatures from solutions which are not saturated at 25° with respect to this salt. This fact makes it very difficult to adjust the whole course of evaporation in such a way that when the hot solution is cooled to 25° it should deposit T. Actually all such attempts have resulted in solutions, the compositions of which lie very near to the point *s* (Fig. 2), which is undoubtedly the crystallisation end-point of the system. In the isothermal evaporation at 25°, the solution remains supersaturated for a considerably long time. In all these cases of evaporation it has been found that crystallisation starts after the process of evaporation has been carried too far. This tendency to form supersaturated solutions has been noticed by van 't Hoff in many cases, particularly those of kieserite, leonite and kainite ($MgSO_4,KCl,3H_2O$) ("Zur Bildung der Ozeanischen Salzablagerungen," 1905, **1**, 28). The present case seems analogous to these and requires similar handling which

necessitates the measurements of the vapour pressure of the hydrated double salt, darapskite, as well as those of the saturated solutions at this temperature (*op. cit.*).

The Isotherm at 90°.—The isotherm at 90° is not so complicated as that at 25°. The only double salt that occurs in the system at this temperature is glaserite. All others seem to break down at temperatures below 90°. In the ternary systems, only the invariant points have been determined, and although the ternary curves have

FIG. 4.



not been followed completely, it is probable that in most cases they are not very different from straight lines. Furthermore, as the quaternary curve l_1x is practically a straight line, there is no doubt that the hydrated double salt, darapskite, in the ternary system H_2O–Na_2SO_4–$NaNO_3$ and the compound T in the quaternary system split up into the simple salts at temperatures lower than 90°. The isotherm is shown in Fig. 4 as the orthogonal projection of the space model, and the data for the system at this temperature are in Table II in terms of molar percentages.

TABLE II.

The System H_2O–Na_2SO_4–$NaNO_3$–K_2SO_4–KNO_3 *at* 90°.

Composition in molar percentages.

Point.	Na_2SO_4.	$Na_2(NO_3)_2$.	K_2SO_4.	$K_2(NO_3)_2$.	Solid phases.
a_1	5·13	—	—	—	Na_2SO_4
l_1	4·98	—	1·25	—	$Na_2SO_4 + D_2$
	1·39	4·72	2·19	—	,,
	—	6·65	2·04	0·41	,,
x	—	14·29	0·64	8·34	$Na_2SO_4 + D_2 + NaNO_3$
y	0·71	13·72	—	—	$Na_2SO_4 + NaNO_3$
f_1	—	14·67	—	—	$NaNO_3$
g_1	—	15·81	—	16·02	$NaNO_3 + KNO_3$
z	—	16·20	0·70	14·96	$NaNO_3 + KNO_3 + D_2$
	—	12·17	0·67	14·78	$KNO_3 + D_2$
h_1	—	—	—	15·26	KNO_3
i_1	—	—	0·16	14·89	$KNO_3 + K_2SO_4$
j_1	—	—	2·37	—	K_2SO_4
k_1	1·49	—	1·97	—	$K_2SO_4 + D_2$
v_1	—	4·16	0·59	14·78	$K_2SO_4 + D_2 + KNO_3$

$D_2 = K_3Na(SO_4)_2$.

The author is indebted to Professor F. G. Donnan for his very kind help and interest during the progress of this work.

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XXXII.—*Preparation, Hydrolysis and Reduction of the Fluoro-, Chloro-, and Bromo-benzyl Bromides.*

By JOHN BALDWIN SHOESMITH and ROBERT HENRY SLATER.

IN previous communications (J., 1922, **121**, 1392; 1923, **123**, 2828; 1924, **125**, 1312, 2278) an account was given of the manner in which the reactivity of halogen atoms in various halogenated benzenoid derivatives is influenced by oxygen and by the hydrogen of a methyl group. The investigations have been continued with a view to discovering the effect of fluorine, chlorine, and bromine in such compounds. From the point of view of the principle of induced alternate polarities the halogens, except fluorine, appear to act as weakly negative "key-atoms" (as pointed out by Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, No. 3). The present investigation has shown that (1) fluorine is capable of inducing differences of reactivity very similar to, but smaller than those met with in the cases of the methoxybenzyl bromides (J., 1922, **121**, 1392) and the ω-bromoxylenes (J., 1924, **125**, 2278) and (2) chlorine and bromine induce still smaller differences, and the chloro- and bromo-benzyl bromides provide the first examples encountered in this series, in

which a change of reagent does not cause a change in the order of reactivity.

The order of ease with which the bromides lose their bromine as bromidion in solution in aqueous alcohol is: (1) *p*-fluorobenzyl bromide > benzyl bromide > *o*-fluoro- > *m*-fluoro-; (2) benzyl bromide > *p*-chloro- > *o*-chloro- > *m*-chloro-; (3) benzyl bromide > *p*-bromo- > *o*-bromo- > *m*-bromo-. The order of ease of reduction by hydriodic acid is: (1) *o*-fluoro- > *m*-fluoro- > benzyl bromide > *p*-fluoro-; (2) *o*-chloro- > *p*-chloro- > *m*-chloro- > benzyl bromide; and (3) *o*-bromo- > *p*-bromo- > *m*-bromo- > benzyl bromide. The differences of ease of hydrolysis are quite marked. Those of ease of reduction are small, but several repetitions of the experiments led to the same order of reactivity and, as is seen from the above, the order of ease of reduction of the chloro- and bromo-compounds is not analogous to that discovered in the cases of the methoxybenzyl bromides, the ω-bromoxylenes, and the fluorobenzyl bromides.

A series of experiments was undertaken to see if this non-reversal of the order of reactivity is due to any of the following causes: (*a*) removal of halogen from the nucleus, (*b*) liberation of iodine as follows: (1) $R{\cdot}C_6H_4{\cdot}CH_2Br + HI \longrightarrow R{\cdot}C_6H_4{\cdot}CH_2I + HBr$. (2) $2R{\cdot}C_6H_4{\cdot}CH_2I \longrightarrow R{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4R$ (compare Silberrad, J., 1924, **125**, 2196), and (*c*) the more rapid formation of the iodide in the case of the para-isomerides and subsequent reduction of the iodides by hydriodic acid. The bromides were reduced for a long time, but the slight elimination of nuclear halogen then noted was not sufficient to reverse the discovered order of reactivity when correction was made for it. Reaction (2) is a photochemical one and does not take place in a dark thermostat such as was used in these experiments. In order to test (*c*), the bromobenzyl iodides were prepared; they were reduced by hydriodic acid at the same rate as the corresponding bromides. Thus it appears as if the conversion of the bromide into iodide is due to a mass-action effect and, owing to the concentration of hydriodic acid used, goes almost equally rapidly in all cases. Some of the iodides lose iodine more rapidly than their isomerides, and when a change in order of reactivity with change of reagent takes place alternating polar influences are very strong, *e.g.*, in the methoxybenzyl bromides.

An approximate estimate of the magnitude of the three influences which affect the reactivity of the bromine atom in the bromides, namely, the general (represented by *g*), the alternating (represented by *a*), and the so-called steric influence (represented by *s*), may be arrived at from considerations similar to those put forward by Flürscheim (J., 1909, **95**, 726). A comparison by means of reaction velocities, which is the most satisfactory method, is impossible,

because only during the hydrolysis of *o*- and *m*-fluorobenzyl bromides and also of the isomeric nitrobenzyl bromides (Shoesmith and Hetherington, J., 1924, **125**, 1316) were the reactions slow enough to give monomolecular velocity coefficients. The reduction of the bromides, moreover, is not the simple bimolecular reaction investigated by West in the case of bromomalonyl compounds (J., 1924, **125**, 710). The reciprocals of the times taken for half-completion of the reaction in the various cases may be used to obtain the necessary comparison.

If K_o, K_m, K_p and K_u represent the reciprocals of the times taken for half-completion of the reactions for the ortho-, meta-, para- and unsubstituted compounds, respectively, the manner in which the velocities of the reactions are affected by the three influences mentioned above may be expressed by the following equations: *

$$\log_{10} K_o = \log_{10} K_u + g + a + s.$$
$$\log_{10} K_m = \log_{10} K_u + g - a.$$
$$\log_{10} K_p = \log_{10} K_u + g + a,$$

and hence

$$g = \tfrac{1}{2}(\log_{10} K_m + \log_{10} K_p - 2 \log_{10} K_u),$$
$$a = \tfrac{1}{2}(\log_{10} K_p - \log_{10} K_m),$$

and $$s = \log_{10} K_o - \log_{10} K_p.$$

Obtained from graphs plotted from observations recorded in this and previous communications, the reciprocals of the various times taken for half-hydrolysis (x) and half-reduction (y) at the temperatures stated are summarised in Table I, on which the following remarks are based:

The general effect. The order in which the atoms or groups affect the reactivity of the bromine (*a*) towards hydrolysing agents in a general way is OMe, Me, F, Cl, Br, CO_2H, NO_2, ranging from the strongly enhancing methoxy-group to the strongly retarding nitro-group, and (*b*) towards hydrogen iodide is OMe and Me, Cl, Br, CO_2H, and F. In the latter case, only the methoxy- and the methyl-group have an appreciable general influence on the reduction velocity. The strong general influence of the methoxy-group is noteworthy.

The alternating effect. The order in which alternation towards hydrolysing agents is produced is similar to that given above (*a*); in this case, however, the magnitudes of the effect may be compared. The order is OMe > F > Me > Cl > Br > CO_2H > NO_2. The differences observed in the first five cases, *i.e.*, negative groups, have positive values, whilst in the last two, *i.e.*, positive groups, they have negative values. For reduction, the order is OMe and Me > CO_2H > F, Cl,

* Logarithms are used in order that the expressions shall finally involve a product or a quotient as the case may be.

TABLE I.

Compounds.	K_o.		K_m.		K_p.		g.		a.		s.	
	x.	y.	x.	y.	x.	y.	Hyd.	Red.	Hyd.	Red.	Hyd.	Red.
Methoxybenzyl bromides.	<33·3 (60°)	0·107 (25°)	0·47	12·5	>33·3*	0·00	>1·54	$+\infty$	0·92	$-\infty$	nil	∞
ω-Bromoxylenes.	2·17 (60°)	>0·00 (25°)†	0·77	0·15	2·78	0·00	0·68	$+\infty$	0·28	$-\infty$	−0·11	∞
Fluorobenzyl bromides.	0·28 (60°)	0·00 (25°)	0·20	0·00	0·91	0·00	−0·39	—	0·33	—	−0·51	—
Fluorobenzyl bromides.	1·0 (76°)	0·27 (101°)	0·71	0·22	4·0	0·18	−0·22	0·00	0·37	−0·05	−0·6	0·18
Chlorobenzyl bromides.	0·85 (76°)	0·36 (101°)	0·65	0·24	1·8	0·31	−0·60	0·27	0·22	+0·05	−0·32	0·07
Bromobenzyl bromides.	0·84 (76°)	0·36 (101°)	0·71	0·23	1·43	0·29	−0·67	0·22	0·15	+0·05	−0·23	0·09
Nitrobenzyl bromides.	0·29 (76°)	—	0·33	—	0·29	—	−1·69	—	0·028	—	nil	—
ω-Bromotoluic acids.	—	—	0·72 (76°)	0·27 (110°)	0·56	0·65	−1·07	+0·06	0·055	+0·19	—	—

Benzyl bromide $x = 0·67$ (60°), 2·17 (76°). $y = 0$ (25°), 0·20 (101°), 0·39 (110°).

* The extraordinary rapidity with which *p*-methoxybenzyl bromide is hydrolysed in aqueous alcoholic solution suggests that this figure should be much greater and hence g and a for hydrolysis approach those for reduction, *i.e.*, ∞

† ω-Bromo-*o*-xylene is definitely but very slowly reduced at 25°. A definite value for $K_o(y)$ cannot be given, but s (red.) must be large on account of the stability of ω-iodo-*p*-xylene at 25° in presence of hydrogen iodide.

and Br. Here the differences in the cases of the OMe, Me and F compounds have positive values and in the other cases negative values. According to the principle of induced alternate polarities the sign of the difference is determined by the positive or negative character of the substituents, and the reduction of the chloro- and bromo-benzyl bromides is the only case so far met with in this series in which the sign of the difference is other than was expected.

The steric effect. The values obtained for *s* show that this effect in some cases diminishes and in other cases increases the reactivity, the former being observed in the hydrolyses, the latter in the reductions. Therefore the retarding of the reactions cannot be due to steric hindrance as normally conceived, and the results justify the conclusion that there is a disturbing factor governing the reactivity of ortho-compounds (see Lapworth and Shoesmith, J., 1922, **121**, 1394).

The influence of atoms or groups of atoms having the same electronic shell may be compared also, since the manner in which the methyl and the methoxy-group and the fluorine atom each affect the reactivity of the bromine atom of the $-C_6H_4\cdot CH_2Br$ group has been investigated. The order of potency is OMe > Me > F, except in the case of alternation of hydrolysis, for which the order is OMe > F > Me.

Experimental.

Preparation of the Isomeric Chlorobenzyl Bromides.—The most reliable method of preparing the ortho- and para-isomerides is indicated by the scheme:

$$C_6H_4Cl\cdot CH_3 \xrightarrow{Cl} C_6H_4Cl\cdot CHCl_2 \xrightarrow{HCO_2H} C_6H_4Cl\cdot CHO$$

$$\downarrow KOH$$

$$C_6H_4Cl\cdot CH_2Br \xleftarrow{HBr} C_6H_4Cl\cdot CH_2\cdot OH$$

The appropriate chlorotoluene, mixed with 5% of its weight of phosphorus pentachloride, was chlorinated at 160° until the required increase in weight had taken place. The oil thus obtained was boiled with twice its bulk of 98% formic acid (*d* 1·20) for ½ hour, the mixture poured into an excess of cold water, and the oil separated, dissolved in ether, washed twice with water, and once with aqueous sodium hydroxide. The aldehyde was precipitated as the bisulphite compound, which was carefully washed with ether, dissolved in water, and the pure aldehyde liberated by the addition of excess of sodium carbonate. It was converted into the alcohol (*o*-, m. p. 70°; *p*-, m. p. 72°) by treatment with 25% alcoholic potassium hydroxide, and this into the bromide by means of hydrogen bromide in benzene solution.

o-*Chlorobenzyl Bromide* is an oil, b. p. 102°/9 mm. (Found: Br, 39·05. C_7H_6ClBr requires Br, 38·9%). *p*-Chlorobenzyl bromide has m. p. 51° (compare Jackson and Field, *Ber.*, 1878, **11**, 905) (Found: Br, 38·7%).

m-*Chlorobenzyl Bromide.*—*m*-Nitrobenzaldehyde was converted into *m*-chlorobenzaldehyde (Erdmann and Schwechten, *Annalen*, 1890, **260**, 59), b. p. 213—214°, and this was reduced to the alcohol in alcoholic potassium hydroxide. The alcohol had b. p. 242°, not 234° as stated by Mettler (*Ber.*, 1905, **38**, 1749), and from it m-*chlorobenzyl bromide*, an oil of b. p. 109°/10 mm. (Found: Br, 38·8%), was obtained as before.

The Isomeric Bromobenzyl Bromides.—Each of these compounds was prepared by passing a stream of air through a weighed quantity of bromine into the appropriate, boiling bromotoluene. The product was distilled under diminished pressure, the portion passing over between 120° and 140°/12—16 mm. being collected, cooled, and when solid recrystallised from alcohol. The bromides thus obtained had m. p.'s: *o*-, 31°; *m*-, 40°; and *p*-, 63° [Found: hydrolysable Br, (*o*-) 32·1, (*m*-) 31·8, (*p*-) 31·8. Calc. for $C_7H_7Br_2$, hydrolysable Br, 32·0%] (compare Jackson, *Ber.*, 1876, **9**, 932).

The *isomeric bromobenzyl iodides* were prepared by boiling aqueous acetone solutions of the corresponding bromides with rather more than the calculated quantity of potassium iodide for ½ hour. The mixture was then poured into water, and the iodide recrystallised from light petroleum. o-*Bromobenzyl iodide* crystallises in shining, white needles, m. p. 47° (Found: I, 42·75. C_7H_6BrI requires I, 42·7%). m-*Bromobenzyl iodide* crystallises in white, six-sided prisms, m. p. 42° (Found: I, 42·8%). *p*-Bromobenzyl iodide crystallises in white needles, m. p. 73° (Hantzsch and Schultze, *Ber.*, 1896, **29**, 2253, give 80—81°) (Found: I, 42·9%).

[With R. H. Slater.]

Preparation of the Isomeric Fluorotoluenes.—A solution of the requisite toluidine (25 g.) in a mixture of 30 c.c. of concentrated sulphuric acid and 80 c.c. of water was cooled to — 5° and diazotised with 20 g. of sodium nitrite dissolved in 50 c.c. of water, the temperature being kept below 5°. The solution of the diazotised base was added to about 400 c.c. of commercial hydrofluoric acid (50—60%) in a 1,500 c.c. brazed spun-copper flask surrounded by ice, after which the flask was fitted, by means of a cork, with a copper reflux condenser and very carefully warmed on a water-bath for about an hour (alternatively, the mixture may be left at room temperature for about 16 hours). The condenser was then reversed and the flask heated directly. The mixture of fluorotoluene, hydrofluoric acid,

and cresol that distilled was collected in a copper beaker containing 300 c.c. of 30% aqueous sodium hydroxide solution surrounded by a good freezing mixture. When all the fluorotoluene had distilled, the *alkaline* mixture in the beaker was extracted thrice with ether, the combined extracts were de-emulsified by saturated ammonium sulphate solution and dried over anhydrous sodium sulphate, and the ether was evaporated. In each case the fluorotoluene distilled at 113—118° and the yield was 15—16 g. (65%) (compare Holleman and Beekman, *Rec. trav. chim.*, 1904, **23**, 238).

Preparation of the Isomeric Fluorobenzyl Bromides.—Each fluorotoluene (80 g. in four lots) was brominated by volatilising bromine (30 g.) in a slow stream of dry air and passing the vapour into the boiling fluorotoluene (20 g.); by using small quantities nuclear substitution was avoided. The brominated oil was boiled with formic acid (*d* 1·20; *ca.* 2 vols.) for 6 hours, fluorobenzotribromide and fluorobenzylidene bromide being thus converted into fluorobenzoic acid and fluorobenzaldehyde, respectively, and some of the fluorobenzyl bromide into fluorobenzyl alcohol. The mixture was poured into a large excess of water, and the oil was separated, and washed in ethereal solution with 10% aqueous sodium hydroxide until free from fluorobenzoic and formic acids. After complete removal of the fluorobenzaldehyde with freshly prepared sodium bisulphite solution—the aldehydes and the benzyl bromides form constant-boiling mixtures—the ethereal solution was dried over anhydrous sodium sulphate, and the ether distilled. The residual oil was saturated in benzene solution with dry hydrogen bromide to convert any fluorobenzyl alcohol into the bromide, and after the removal of the benzene the fluorobenzyl bromide was fractionally distilled in a vacuum in the apparatus described by Widmer (*Helv. Chim. Acta*, 1924, **7**, 52). o-*Fluorobenzyl bromide* had b. p 84—85°/15 mm.; m-*fluorobenzyl bromide*, 77°/12 mm.; and p-*fluorobenzyl bromide*, 85°/15 mm. [Found: Br, 42·4 (*o*-); 42·0 (*m*-); 42·1 (*p*-). C_7H_6FBr requires Br, 42·3%].

Hydrolysis of the Bromides.—Twenty c.c. of a standard solution (105 c.c.) of the bromide in absolute alcohol were placed in a standard 25 c.c. flask, 5 c.c. of water added, and the volume was made exactly 25 c.c. by adding absolute alcohol. The whole was thoroughly mixed, immersed in the vapour of boiling carbon tetrachloride for a definite time, and then poured into a large volume of water. The liberated hydrobromic acid was titrated directly with standard aqueous sodium hydroxide and methyl-red. The results are in Table II, where w represents the total weight of benzyl bromide used, x the percentage changed, and t the time of hydrolysis in hours.

TABLE II.

	Ortho-compounds.			Meta-compounds.			Para-compounds.		
F:	$w = 0{\cdot}5218$ g.			0·5456 g.			0·5102 g.		
Cl:	0·5600 ,,			0·5441 ,,			0·5418 ,,		
Br:	0·6702 ,,			0·6600 ,,			0·6693 ,,		
	x.			x.			x.		
t.	F.	Cl.	Br.	F.	Cl.	Br.	F.	Cl.	Br.
½	25	25	24	24	21	21	68	45	40
1	51	46	44	41	38	39	88	69	62
2	76	68	66	63	58	60	96	88	85
4	94	88	87	86	80	82	98	96	95
8	95	96	96	94	92	95	99	98	98

In Table III are results obtained in a similar manner in order to compare the hydrolysis of benzyl bromide, *m*-methoxybenzyl bromide,* the fluorobenzyl bromides, and the ω-bromoxylenes at 60·5° (b. p. of chloroform).

TABLE III.

	Fluorobenzyl bromides.			*m*-Methoxybenzyl bromide.	Benzyl bromide.
	o.	*m*.	*p*.		
w.	0·5240	0·5252	0·5102	0·543	0·4610
t.	x.	x.	x.	x.	x.
½	9	7	26·5	14	22
1	20	11	48	29	39
2	33	23	69	49	59
4	56	41	90	72	80
8	76	63	95	88	88
16	91	81	96	—	—

Reduction of the Bromides.—Reduction at 25° under the conditions described by Lapworth and Shoesmith and by Shoesmith and Slater (*loc. cit.*) being so slow that satisfactory results could not be obtained, the bromides were reduced in a thermostat at 101°. Ten c.c. of a standard solution of the bromide in 50 c.c. of glacial acetic acid were placed in the 25 c.c. standard flask, 10 c.c. of freshly distilled hydriodic acid (*d* 1·680) added, the volume was made up to 25 c.c. with glacial acetic acid, and the whole thoroughly mixed, and kept in the thermostat for a definite time. The percentage reduction was then estimated as in previous cases.

The concentration of the hydriodic acid and the amount of iodine in it both influence the rate of reduction, and therefore a series of reductions was carried out on the same day with the same hydriodic acid. The results are in Table IV, t and x having the same significance as before.

* At all temperatures, in aqueous alcoholic solution, *p*-methoxybenzyl bromide is completely, and the *o*-compound almost completely, hydrolysed in 2½ minutes.

TABLE IV.

	Ortho-compounds. x.			Meta-compounds. x.			Para-compounds. x.		
t.	F.	Cl.	Br.	F.	Cl.	Br.	F.	Cl.	Br.
$1\frac{1}{2}$	29·5	32	30 (31)	23	23	23 (21)	22·5	28	26 (27)
3	45	53	53 (54)	37	43	43 (41)	34	49	47 (47)
6	65	76	74 (76)	63	64	61 (60)	57	68	64 (65)

Benzyl bromide : $x = 25$, 38, and 61 for $t = 1\frac{1}{2}$, 3, and 6, respectively.

The figures in brackets represent the reduction of the bromobenzyl iodides. In Table V are the results of reductions of the bromides made at a higher temperature (110°) in order to determine the amount of nuclear halogen eliminated.

TABLE V.

	Ortho-compounds. x.		Meta-compounds. x.		Para-compounds. x.	
t.	Cl.	Br.	Cl.	Br.	Cl.	Br.
2	76	77	57	57	70	72
4	91	91	81	79	88	88
8	102	100	97	97	98	97
18	104	103	100	100	101	101

p-Chlorobenzyl iodide (m. p. 65°) was isolated from the reaction of *p*-chlorobenzyl bromide and hydrogen iodide in glacial acetic acid at 25° (compare Shoesmith and Slater, *loc. cit.*), but, owing to the dilution at which the reductions had to be carried out, end-products in the other cases could not be separated. The figures obtained, however, show that the reaction in the cases of the meta- and para-isomerides was quite normal in that it first involved conversion of the bromide into iodide and subsequent reduction of this to the halogenated toluene.

The iodobenzyl bromides have not been examined, since in a former communication we showed that hydrogen iodide reduces iodotoluene to toluene.

The authors gratefully acknowledge the many valuable suggestions made by Dr. W. O. Kermack, especially with regard to the formulæ on pp. 216, and the receipt of a grant from the Earl of Moray Research Fund. They also thank the Trustees of the Carnegie Trust for the Universities of Scotland for a scholarship which enabled one of them (R. H. S.) to take part in this research.

UNIVERSITY OF EDINBURGH. [*Received, December 3rd*, 1925.]

XXXIII.—*Cyclic Organo-metallic Compounds. Part I. Compounds of Tellurium.*

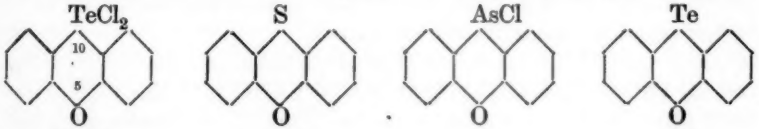
By HARRY DUGALD KEITH DREW.

THE present work has for its object the investigation of cyclic organo-metallic compounds (*i.e.*, compounds in which a metallic atom is united directly to carbon atoms, taking part therewith in ring formation), few of which have hitherto been synthesised.

Tellurium tetrachloride and diphenyl ether slowly but almost completely condense when heated together in chloroform solution. Hydrogen chloride is evolved and a yellow telluritrichloride is formed in which the group $-TeCl_3$ has replaced a hydrogen atom of one of the aromatic nuclei. This substance is p-*phenoxyphenyltelluritrichloride* (I), $PhO{\cdot}C_6H_4{\cdot}TeCl_3$, since on reduction with aqueous potassium metabisulphite it becomes transformed to a purplish-red, crystalline substance, pp′-*diphenoxydiphenyl ditelluride* (II), $PhO{\cdot}C_6H_4{\cdot}Te{:}Te{\cdot}C_6H_4{\cdot}OPh$, which shows a normal molecular weight in freezing benzene.

The formation of these substances demonstrates that the tellurium atom can be caused to enter an aromatic nucleus without the aid of Grignard reagents (compare Morgan and Drew, J., 1925, **127**, 2307). That the group $-TeCl_3$ enters the aromatic nucleus almost exclusively in one position was shown by the absence of an isomeric telluritrichloride from the by-products of this condensation and by the homogeneity of the ditelluride resulting upon reduction.

The telluritrichloride (I) melts at 156°, but if it is heated to about 200° a further (intramolecular) condensation occurs; a molecule of hydrogen chloride is evolved, and a colourless, crystalline, cyclic compound, 10 : 10-*dichlorophenoxtellurine* (III), is produced. That this substance contains the tellurium atom in a di-ortho-position relatively to the oxygen atom is indicated both from stereochemical considerations and by the existence of structurally analogous compounds of sulphur (IV) and of arsenic (V), of which the constitutions must be regarded as established (compare, for

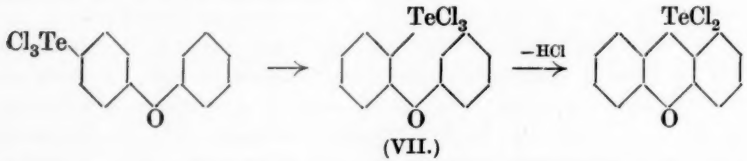


(III.) (IV.) (V.) (VI.)

example, Turner and Sheppard, J., 1925, **127**, 544). Additional evidence upon this point is afforded by the ready reduction of the telluridichloride (III) to a yellow, crystalline, cyclic substance, *phenoxtellurine* (VI), of such marked chemical and physical stability

that there seems no doubt as to the nature of its tricyclic structure. This substance, which shows a normal molecular weight in freezing benzene, resembles somewhat closely the colourless sulphur analogue, phenoxthin or phenothioxin (IV; Mauthner, *Ber.*, 1906, **39**, 1344), in both physical and chemical properties. It has, for example, a delicate floral odour suggesting rose-water, whereas phenoxthin is described as having a geraniol smell; and both substances develop intense colorations with concentrated sulphuric acid. Phenoxtellurine readily adds on bromine or iodine in chloroform solution, yielding primrose-yellow 10 : 10-*dibromophenoxtellurine* and red 10 : 10-*di-iodophenoxtellurine*, respectively; while the action of warm nitric acid converts it into colourless *phenoxtellurine* 10 : 10-*dinitrate*.

The formation of a cyclic tellurium compound from the telluritrichloride (I) suggests that the latter must in reality be the *o*-compound (VII). Since, however, it has been shown (Morgan and Drew, *loc. cit.*) that in the analogous condensation with phenetole the group $-TeCl_3$ takes up exclusively a para-position with respect to ethoxyl, a para-orientation with respect to the phenoxy-group in the present case also would be anticipated. There remains thus the probability that the telluritrichloride is actually the *p*-compound (I), and that, on being heated above its melting point, it suffers a preliminary isomeric change into the *o*-compound (VII), which can then undergo the inner condensation :—



(VII.)

In an endeavour to test this possibility, the action of concentrated nitric acid upon the ditelluride (II) was tried. The telluritrinitrate, $PhO{\cdot}C_6H_4{\cdot}Te(NO_3)_3$, was first produced and then the tellurium atom displaced, *pp'*-dinitrodiphenyl ether (m. p. 143°) being formed; no *o*-nitro-compound was isolated. Of the two obvious mechanisms of displacement of the tellurium atom, *viz.*,

(1) $PhO{\cdot}C_6H_4{\cdot}Te(NO_3)_3+HO{\cdot}NO_2=Te(NO_3)_3{\cdot}OH+PhO{\cdot}C_6H_4{\cdot}NO_2$,
and (2) $PhO{\cdot}C_6H_4{\cdot}Te(NO_3)_3 + H{\cdot}NO_3 = Te(NO_3)_4 + PhO{\cdot}C_6H_5$, the more probable would appear to be (1); and, if this is the case, the production of a *p*-nitro-compound of diphenyl ether proves the structure of the telluritrichloride and of the ditelluride derived from it. The possibility of mechanism (2), in which diphenyl ether is first liberated and then nitrated, cannot, however, be ignored with safety.

On the whole, the weight of evidence seems to be in favour of the para-structure; and accordingly it is considered best to adopt, for the present, the formulæ I and II for the telluritrichloride and ditelluride respectively, and to assume the transformation of the *p*-telluritrichloride into its *o*-isomeride as an intermediate step in the synthesis of the cyclic dichloride (III).

The best method of preparing 10 : 10-dichlorophenoxtellurine, giving a yield of 50%, is to heat at about 200° a mixture of tellurium tetrachloride and diphenyl ether in molecular proportions. The reaction proceeds in two stages, marked evolution of hydrogen chloride occurring first near 120° and then again near 200°. These stages apparently represent respectively the formation of the telluritrichloride and its transformation to the cyclic telluridichloride. The hypothetical preliminary isomeric change of the *p*- to the *o*-telluritrichloride must then occur between the temperature of the melting point of the telluritrichloride and the higher temperature, *i.e.*, between about 160° and 200°, a separate experiment having shown that the presence of chloroform in the preliminary stages of the above reaction had no effect upon the nature of the ultimate product.

Accordingly, an attempt was made to isolate the *o*-telluritrichloride by heating the supposed *p*-telluritrichloride to about 160° in an atmosphere of nitrogen. From the glassy product, which was a complex mixture containing a proportion of regenerated tellurium tetrachloride, a substance was obtained which had the properties of a telluritrichloride and yet was not identical with the initial material. This compound, which crystallised from benzene in almost colourless, pearly flakes decomposing at 125°, was possibly the *o*-telluritrichloride (VII), since it was easily reduced to a red substance possessing the characteristics of a ditelluride. Neither of these compounds was obtained in a pure condition, however, and their identity with the above structures has not been definitely established.

A colourless non-cyclic telluridichloride occurs as a by-product in the condensation of tellurium tetrachloride and diphenyl ether in chloroform solution; and this substance results also when the telluritrichloride (I) is heated with an excess of diphenyl ether at about 160°, hydrogen chloride being set free. This telluridichloride must therefore be pp'-*diphenoxydiphenyltelluridichloride* (VIII), $PhO{\cdot}C_6H_4{\cdot}TeCl_2{\cdot}C_6H_4{\cdot}OPh$.

Here again the di-para-orientation is considered the more probable, since the substance is formed in small amount even at the low temperature of a condensation in chloroform. Owing, however, to the uncertainty attaching to the conditions under which the hypothetical

change of the tellurium atom from the *p*- to the *o*-position occurs, a di-ortho-, or even a para-ortho-structure is not definitely excluded.

The non-cyclic telluridichloride (VIII) was unchanged by the action of heat at 210°, and its formation was therefore unconnected with the production of the cyclic telluridichloride (III). It was of interest, therefore, to find that the latter was the main product of the action of heat at 200° upon a mixture of tellurium tetrachloride and a large excess (3½ mols.) of diphenyl ether, for this result seems to supply further evidence in favour of the hypothetical isomeric change of the *p*- to the *o*-telluritrichloride; since, in the absence of this transformation, it would be expected that the whole of the telluritrichloride would be changed at 200° into the non-cyclic telluridichloride (VIII), a reaction which is fairly rapid even at 160°. The production of the *o*-telluritrichloride must therefore accelerate rapidly at temperatures approaching 200°.

Leaving aside the question of orientation, we have thus the following series of changes which have been realised experimentally, with the temperatures at which the reactions are appreciably rapid :—

$$TeCl_4 + C_6H_5\cdot OPh \xrightarrow[(\text{with or without } CHCl_3)]{120^\circ} HCl + TeCl_3(C_6H_4\cdot OPh);$$

$$TeCl_3(C_6H_4\cdot OPh) + C_6H_5\cdot OPh \xrightarrow{160^\circ} HCl + TeCl_2(C_6H_4\cdot OPh)_2;$$

$$TeCl_3(C_6H_4\cdot OPh) \xrightarrow{200^\circ} HCl + TeCl_2(C_6H_4\cdot O\cdot C_6H_4);$$

$$TeCl_4 + C_6H_5\cdot OPh \xrightarrow{200^\circ} 2HCl + TeCl_2(C_6H_4\cdot O\cdot C_6H_4).$$

It is probable that *pp'*-diphenoxydiphenyltelluridichloride (VIII) is always formed, at least in minor quantities, when tellurium tetrachloride and diphenyl ether are heated together; but this telluridichloride is not readily separated from the resinous or colloidal by-products associated with it in the reaction-mixture.

Attempts are being made to clear up the uncertainty which exists regarding the orientations of the foregoing substances; and, in addition, the author is investigating the analogues and derivatives of phenoxtellurine and similar compounds containing other metals and metalloids.

EXPERIMENTAL.

Condensation of Tellurium Tetrachloride with Diphenyl Ether in presence of Chloroform.—Four experiments were carried out, with proportions of diphenyl ether ranging from 1 to 1½ mols. per mol. of tellurium tetrachloride and with amounts of chloroform varying between 0·6 and 2 c.c. per g. of the tetrachloride; the times of heating were between 8 and 26 hours. The optimum experiment only will be described in detail: 23·8 g. of tellurium tetrachloride, 18·7 g.

(1¼ mols.) of diphenyl ether, and 15 c.c. of dry chloroform were heated under reflux during 26 hours, moist air being excluded. Hydrogen chloride was evolved and all the tellurium tetrachloride dissolved in about 1½ hours. The yellow trichloride that was gradually deposited from the intensely orange-brown solution was recrystallised from boiling dried chloroform; the mother-liquor on concentration to a syrup gave further crops of trichloride, which were recrystallised as before (total yield, 31·5 g. or 90%). The final syrup, on long standing in a desiccator, gave the dichloride (0·5 g.) in large, colourless prisms, which were recrystallised from ethyl alcohol or acetone. In this and in other experiments the separating trichloride was practically pure. Portions of it were subjected to careful fractionation from boiling dry chloroform, in an attempt to detect the presence of a possible isomeric trichloride. The melting points and mixed melting points of the recrystallised first and final fractions were always practically identical. Slight differences sometimes observed were traced to the presence of small amounts of the dichloride.

p-*Phenoxyphenyltelluritrichloride* (I) separates from its yellow solution in chloroform or carbon tetrachloride in opaque, nodular rosettes of very small, pale yellow needles. The rosettes crumble, on drying, to a creamy yellow, crystalline powder. The substance melts at 156—157° to a transparent, yellow liquid, but never quite sharply, usually softening from about 154°, behaviour which suggests a partial change near the melting point. The compound is almost insoluble in light petroleum, sparingly soluble in hot carbon tetrachloride, but more soluble in hot chloroform or benzene. It is readily hydroxylated by water or hydroxylic organic solvents (Found: C, 35·6; H, 2·3; Cl, 26·6. $C_{12}H_9OCl_3Te$ requires C, 35·75; H, 2·25; Cl, 26·4%).

pp′-*Diphenoxydiphenyltelluridichloride* (VIII), a by-product in the foregoing condensation, was best prepared by heating 3·9 g. (1 mol.) of the above trichloride and 1·7 g. (1 mol.) of diphenyl ether together at 140—165° during 6 hours, moist air being excluded and a slow current of nitrogen maintained in the apparatus. Hydrogen chloride was evolved even at 145°. The hard, semi-crystalline mass was extracted with ether, the ether removed, and the resulting semi-solid triturated successively with light petroleum and ethyl alcohol, and filtered. There remained 2·8 g. of crude dichloride containing an amorphous impurity, readily soluble in chloroform, benzene or acetone, from which it was found difficult to free the dichloride. Purification was finally effected by fractional solution in cold benzene, followed by crystallisation of the least soluble fraction from benzene–light petroleum (b. p. 40—60°).

When two molecular proportions of diphenyl ether were employed and the heating was conducted during 10 hours at 115—150°, a similar product (1·1 g. from 1·5 g. of trichloride) was obtained, which yielded the dichloride on purification by means of carbon tetrachloride and ether. When quite pure, the dichloride separated from boiling methyl or ethyl alcohol in transparent, colourless, prismatic needles, which became slightly pink on keeping. The solutions in hot alcohol of impure specimens always became cloudy, on cooling, before crystallisation set in. The dichloride melted without decomposition at 157—158°, and depressed the almost identical melting point of the trichloride to about 120°. It was much more easily soluble than the trichloride in organic solvents, being readily soluble in cold benzene, chloroform or ether; but it was insoluble in light petroleum, and only moderately easily soluble in hot ethyl alcohol. The halogen atoms were firmly bound in this substance, which remained unaffected by cold aqueous potash, although it was decomposed by the boiling reagent with liberation of diphenyl ether (Found: Cl, 13·15. $C_{24}H_{18}O_2Cl_2Te$ requires Cl, 13·2%).

When this dichloride was heated at 210° during an hour, it remained unchanged, no trace of diphenyl ether or of cyclic telluridichloride being produced.

pp′-*Diphenoxydiphenyl Ditelluride* (II).—The trichloride (7 g.) was reduced with 50 c.c. of ice-cold water and 11·6 g. (3 mols.) of powdered potassium metabisulphite, which was slowly added during ¾ hour, the mixture being stirred mechanically. Sulphur dioxide was evolved, and a soft red mass produced. The reduction was completed by grinding the whole in a glass mortar during a further ½ hour. The deep purple, crystalline product was filtered off, washed with water, and dried in a vacuum; the yield of crude product (5·3 g.) was quantitative. The substance was then rapidly crystallised from hot light petroleum (b. p. 40—60°) saturated with sulphur dioxide, two crystallisations producing the analytically pure ditelluride. Careful examination of the mother-liquors failed to reveal the presence of an isomeride.

pp′-*Diphenoxydiphenyl ditelluride* separates from petroleum or alcohol in clusters of minute, bronzed, brownish-violet or purplish-red needles, which dissolve in organic solvents to dark red solutions. It commences to soften at 85° and melts to a deep red liquid at 87—88°. It is easily soluble in benzene, chloroform, carbon tetrachloride, ether, or acetone, only moderately easily soluble in light petroleum or alcohol, and insoluble in water [Found: C, 48·55; H, 3·05; Te, 43·1; *M*, cryoscopic in benzene, 579 ($c = 1·39$), 595 ($c = 2·04$). $C_{24}H_{18}O_2Te_2$ requires C, 48·55; H, 3·05; Te, 43·0%; *M*, 593].

Great difficulty was at first experienced in purifying this substance sufficiently for analysis. Although it crystallised well from ethyl or methyl alcohol and from acetone or ether, the crystals were persistently low in carbon content (Found: C, 47·6, 47·6, 47·5, 48·05; H, 3·1, 3·2, 3·1, 3·15%). Finally the impurity was isolated: it consisted of a white, amorphous oxide, which was slowly reduced by aqueous potassium metabisulphite or aqueous sulphur dioxide to the ditelluride. In solution the ditelluride slowly precipitates this oxide when exposed to the air. With bromine in cold chloroform solution the ditelluride reacts to form a yellow *bromide* melting near 180° and readily soluble in hot chloroform. This substance is probably the analogue of the trichloride, since it is again reduced to the ditelluride by aqueous alkali bisulphites. With warm concentrated nitric acid the ditelluride yields ultimately *pp'*-dinitrodiphenyl ether (needles from alcohol; m. p. 142—143°).

Preparation of 10 : 10-*Dichlorophenoxtellurine.*—(1) *Action of heat on* p-*phenoxyphenyltelluritrichloride.* The trichloride (1·4 g.) was heated gradually during $4\frac{3}{4}$ hours, from 150° to 210°; hydrogen chloride was slowly evolved. The cooled melt was extracted with ether; a substance sensitive to moisture (probably tellurium tetrachloride) was then found to be present. The residue from the ether extraction, on crystallisation from boiling toluene, yielded 0·4 g. (or 33%) of the pure cyclic telluridichloride, identical with the following product in (2).

When the trichloride (5·6 g.) was heated at a lower temperature (150—160°) during 2 hours in a current of nitrogen, a lesser proportion of hydrogen chloride was evolved. On cooling, the melt solidified to a brown glass, which was powdered and dissolved in hot dry chloroform. The solution, kept out of contact with moist air, deposited pale pinkish-white micro-needles (0·5 g.) of a telluritrichloride (probably corresponding with formula VII) which, however, still contained traces of tellurium tetrachloride (Found: Cl, 27·3; whereas formula VII requires Cl, 26·4%). Recrystallised from hot benzene, the compound formed a voluminous mass of almost colourless, nacreous flakes, decomposing near 125° with darkening and evolution of hydrogen chloride. It was readily reduced by aqueous potassium metabisulphite to a red substance (probably the ditelluride), which was soluble in benzene but easily oxidised by the air, while in solution, to a less soluble substance.

The main product of the above reaction was a glutinous mixture containing free tellurium tetrachloride.

(2) *Action of heat upon an equimolecular mixture of tellurium tetrachloride and diphenyl ether.* Six experiments under varying condi-

tions were carried out, but the yield of cyclic dichloride seemed almost constant (about 50%). The following is a typical experiment: Tellurium tetrachloride (11·1 g.) and diphenyl ether (7·0 g.) were heated together in a flask with a long air-condenser, carrying a moisture guard-tube, a slow current of nitrogen being bubbled through the melt (this was not essential, however). The temperature was raised slowly from 100° to 240° over a period of 13 hours, when hydrogen chloride was evolved, mainly during two maximal phases, the first occurring near 120° and the second near 200°. The melt gradually thickened and after about 8 hours partly solidified even at 190°, but remelted as the temperature rose. The cooled melt finally set to a crystalline cake, which was ground to a loose brown powder. The powder was stirred with ether, filtered off, dissolved in acetone, and filtered from 0·8 g. of free tellurium. Evaporation of the acetone left 9·4 g. of the fairly pure cyclic dichloride (62%); but, on further purification of the product in a Soxhlet apparatus with toluene, the yield fell to 48%.

Keeping the temperature below 220°, reducing the time of heating to 5 hours, adding a little chloroform at the commencement of heating, and other similar modifications produced no important variation in the yield.

The material obtained by evaporating the ethereal extracts of the product contained free diphenyl ether or chlorinated diphenyl ether, as well as soluble tellurium compounds which could not be isolated from the viscous residues.

10 : 10-*Dichlorophenoxtellurine* (III) crystallises from boiling toluene in colourless, nacreous platelets, which melt without decomposition at 265° to a transparent, yellow liquid. At 100° the crystalline solid is yellow, but reverts to the colourless form on cooling. It is extremely stable to heat and can be vaporised without undergoing much decomposition; is almost insoluble in ether or petroleum, sparingly soluble in chloroform or ethyl alcohol, rather more soluble in benzene or toluene, and easily soluble in acetone. It is slowly hydrolysed by boiling water, a white oxide resulting. Boiling aqueous potash detaches the tellurium atom and generates diphenyl ether. The solution in cold concentrated sulphuric acid is yellow (Found: C, 39·8; H, 2·2; Cl, 19·3. $C_{12}H_8OCl_2Te$ requires C, 39·3; H, 2·2; Cl, 19·35%).

Phenoxtellurine (VI).—The powdered dichloride (4 g.) was reduced at 0° with 25 c.c. of water and 4·8 g. (2 mols.) of potassium metabisulphite, slowly added with stirring, when sulphur dioxide was evolved. The yellow product was ground beneath the liquid in a glass mortar during an hour to complete the reduction, and the solid was then filtered off, washed with water, and dried. The

yield (3·2 g.) was nearly theoretical. The product was recrystallised from light petroleum (b. p. 40—60°).

Phenoxtellurine separates from hot petroleum in long, spear-like needles and from the cold solvent in large, transparent prisms, both forms being lemon-yellow to orange in colour, melting without decomposition at 78—79°, and having a delicate floral odour. The compound is very stable to heat and can be vaporised unchanged. It is insoluble in water, but easily soluble in ethyl alcohol, ether, benzene, or carbon tetrachloride to yellow solutions. It dissolves in cold concentrated sulphuric acid to a deep purplish-red solution, and is stable towards hot concentrated hydrochloric acid or dilute aqueous caustic soda [Found: C, 48·7; H, 2·9; Te, 43·4; *M*, cryoscopic in benzene, 287 ($c = 1·25$), 294 ($c = 2·18$). $C_{12}H_8OTe$ requires C, 48·7; H, 2·7; Te, 43·1%; *M*, 295·5].

Warm concentrated nitric acid does not immediately cause nuclear nitration of phenoxtellurine, but produces the 10 : 10-*dinitrate*, which forms colourless needles decomposing near 258°. Bromine and iodine in chloroform solution readily yield respectively the 10 : 10-*dibromide*, bright yellow spangles from chloroform or primrose-yellow prisms from toluene (decomposing at 290°), and the 10 : 10-*di-iodide*, red spangles (decomposing indefinitely, mainly near 270°).

Action of Heat upon Mixtures of Tellurium Tetrachloride and Diphenyl Ether in Various Proportions.—(1) When it was attempted to introduce two $-TeCl_3$ groups into the molecule of diphenyl ether by using 2 mols. of tellurium tetrachloride to 1 mol. of the aromatic ether and heating at 120° during 6 hours, only the telluri-trichloride was obtained, part of the tellurium tetrachloride remaining unaltered.

(2) Tellurium tetrachloride and 2 mols. of diphenyl ether, heated at 110° to 180° during 8 hours, yielded only a mixture of a trichloride and the cyclic dichloride.

(3) Tellurium tetrachloride (1 mol.) and diphenyl ether (3½ mols.), heated at 110° to 210° during 16 hours, gave a yield of 42% of 10 : 10-dichlorophenoxtellurine, showing that the tendency towards formation of this cyclic dichloride is maintained even in presence of a large excess of diphenyl ether.

The author's thanks are due to Professor Morgan for his kind interest in the work and for his gift of certain research chemicals.

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XXXIV.—*The Quaternary Salts of Benzoxazoles.*

By LESLIE MARSHALL CLARK.

SINCE the pseudo-bases of the quaternary salts of substituted benzthiazoles have been shown to be *o*-acylmethylaminothiophenols (Mills, Clark, and Aeschlimann, J., 1923, **123**, 2354; Clark, J., 1925, **127**, 973), the corresponding benzoxazole compounds have now been investigated so that a comparison may be made between the properties of these analogous ring systems.

Benzoxazole methiodide was first prepared by Fischer (*J. pr. Chem.*, 1906, **73**, 435), who showed that when the salt was heated with hydrochloric acid, *o*-methylaminophenol was formed, whilst treatment with hot alkalis caused profound decomposition.

It has now been found that benzoxazole methiodide, on being dissolved in water, gives a solution, acid to litmus, from which, after addition of one equivalent of caustic alkali, *o*-formylmethylaminophenol can be obtained. In the same way, 1-methylbenzoxazole methiodide * and 1-phenylbenzoxazole methiodide readily hydrolyse in aqueous solution to *o*-acetylmethylaminophenol and *o*-benzoylmethylaminophenol, respectively, with the liberation of one equivalent of acid.

The reaction is therefore to be represented by the equation

$$C_6H_4\langle\begin{matrix}O\text{—}\\ NMeI\end{matrix}\rangle CR + H_2O = C_6H_4\langle\begin{matrix}OH\\ NMe\cdot COR\end{matrix} + HI$$

No such effect is apparent in these quaternary salts as was observed by Skraup (*Annalen*, 1919, **419**, 80), who found that in the 1-substituted benzoxazole bases resistance of the oxazole ring to fission increases with increasing volume of the substituent radical.

Attempts to reverse the hydrolysis were made by passing dry hydrogen iodide through a solution of *o*-benzoylmethylaminophenol in dry ether and by dissolving *o*-acetylmethylaminophenol in excess of concentrated perchloric acid. The hydriodide of the acylmethylaminophenol separated in the first case, but no 1-phenylbenzoxazole methiodide was obtained, and in the second the only substance isolated was the unchanged phenol.

There appeared to be some possibility that the complete scheme

* Since this paper was prepared for publication, Konig and Meier (*J. pr. Chem.*, 1925, **109**, 324) have shown that 1-methylbenzoxazole methiodide on hydrolysis with water gives *o*-acetylmethylaminophenol.

for the action of alkalis on substituted benzoxazole quaternary salts might be represented thus:

$$C_6H_4\!<\!\overset{O}{\underset{NMeI}{}}\!>\!CR \rightarrow C_6H_4\!<\!\overset{O}{\underset{NMe}{}}\!>\!CR\cdot OH \rightarrow C_6H_4\!<\!\overset{OH}{\underset{NMe\cdot COR}{}}$$
(I.) (II.)

Were this the case, methylation might be expected to yield a derivative of each of the compounds I and II. On treating an aqueous solution of 1-phenylbenzoxazole methiodide with a slight excess of sodium hydroxide and methyl sulphate, only *o*-benzoylmethylaminoanisole could be isolated, whose identity was established by synthesis in the following stages:

$$C_6H_4\!<\!\overset{OMe}{\underset{NO_2}{}} \rightarrow C_6H_4\!<\!\overset{OMe}{\underset{NH_2}{}} \rightarrow C_6H_4\!<\!\overset{OMe}{\underset{NHMe}{}} \rightarrow C_6H_4\!<\!\overset{OMe}{\underset{NMe\cdot COPh}{}}$$

Under these conditions, therefore, no evidence for the presence of the carbinol base (I) is obtained. Although there is thus a measure of similarity between benzoxazolonium and benzthiazolonium salts in their reactions with alkalis, two important differences must be noticed:

(*a*) Benzoxazolonium salts are hydrolysed by water alone, whereas benzthiazolonium salts are stable in aqueous solution.

(*b*) In consequence of this behaviour, benzoxazole quaternary salts cannot be obtained by treatment of the *o*-acylmethylaminophenols with acids, whereas benzthiazole methiodide is readily recovered from the sodium salt of formylmethylaminothiophenol (Mills, Clark, and Aeschlimann, *loc. cit.*).

Experimental.

Benzoxazole Methiodide.—Benzoxazole was prepared by Ladenburg's method (*Ber.*, 1876, **9**, 1924) by heating together *o*-aminophenol and formic acid. Fischer (*loc. cit.*) obtained the methiodide by heating the base with excess of methyl iodide at 100° for 3 hours, and describes it as yellow, shining needles, m. p. 182° (decomp.). In this investigation, the two substances were combined at temperatures varying from 50° to 100°; the product was similar in colour to Fischer's but melted at 202° (decomp.). The purest material was obtained by heating the base with 10% excess of methyl iodide at 60° for 8 hours and extracting the crushed product with dry ether (Found: C, 37·1, 37·25; H, 3·0, 3·1; N, 5·2; I, 48·8. Calc., C, 36·8; H, 3·1; N, 5·4; I, 48·6%).

Action of Potassium Hydroxide on Benzoxazole Methiodide.—From mixed aqueous solutions of the methiodide (10 g.) and potassium hydroxide (rather more than 1 equiv.), *o*-formylmethylaminophenol crystallised on cooling, and a further crop was

obtained by passing carbon dioxide through the mother-liquor. It crystallised from benzene in colourless needles (yield, 5 g.), m. p. 103—104° (Found: C, 63·6; H, 5·8; N, 9·0. Calc., C, 63·6; H, 6·0; N, 9·3%).

The *formyl* compound (1 g.) was heated for 1 hour with concentrated hydrochloric acid (7·5 c.c.) and water (4 c.c.), the solution made slightly alkaline with sodium hydroxide, and the alkali neutralised with carbon dioxide; 0·7 g. of almost colourless, shining flakes of *o*-methylaminophenol was obtained, m. p. 95—96° (Lees and Shedden, J., 1903, **83**, 756, give m. p. 96—97° and Fischer, *loc. cit.*, gives m. p. 86—87°).

For further characterisation of the product, a nitroso-derivative was prepared by Dieppolder's method (*Ber.*, 1899, **32**, 3519) from this compound, and from an authentic specimen of *o*-methylaminophenol. Both nitroso-derivatives and their mixture crystallised from alcohol in colourless, glistening plates, m. p. 125—126° (decomp.) (Found: N, 18·0. Calc., N, 18·4%).

1-*Methylbenzoxazole Methiodide.*—1-Methylbenzoxazole, prepared by Ladenburg's method (*Ber.*, 1876, **9**, 1524), was heated (13·5 g.) with methyl iodide (17 g.) for 8 hours at 100°. The yellow mass was extracted with dry ether and crystallised from acetone in colourless needles, which became light brown unless rapidly dried; m. p. 196° (decomp.) (Found: C, 39·5; H, 3·6; I, 46·1. Calc., for $C_9H_{10}ONI$, C, 39·3; H, 3·6; I, 46·2%).

1-*Methylbenzoxazole Methoperchlorate.*—The methiodide was dissolved in a little cold water and treated with excess of a saturated solution of sodium perchlorate. A mass of colourless plates was immediately precipitated, m. p. 165—170°. Recrystallisation from water lowered the melting point to 150—160°, evidently causing decomposition. A portion of the crude perchlorate was extracted with ether, whereby the hydrolysis product, *o*-acetylmethylaminophenol, m. p. 150°, was removed. The purified *perchlorate* had m. p. 173°, unchanged by crystallisation from acetone–ether (Found: N, 6·0. $C_9H_{10}O_5NCl$ requires N, 5·7%).

The salt (0·8 g.) was heated in aqueous solution for 1½ hours; colourless needles of *o*-acetylmethylaminophenol, m. p. 151°, crystallised on cooling (Found: N, 8·8. Calc., N, 8·5%).

1-Methylbenzoxazole methiodide in aqueous solution at laboratory temperature was hydrolysed incompletely after 8 hours and completely after 66 hours.

Action of Potassium Hydroxide on 1-*Methylbenzoxazole Methiodide.*—The reaction was carried out in the same way as for benzoxazole methiodide. The yield of *o*-acetylaminophenol, m. p. 151°, from 7 g. of salt was 2·1 g.

Action of Silver Oxide on 1-*Methylbenzoxazole Methiodide.*—The salt (1 g.) was dissolved in acetone (300 c.c.) and silver oxide freshly prepared from silver nitrate (3 g.) was added. Silver iodide was formed and after being shaken for 1 hour the acetone solution was evaporated: the residue was crystallised from benzene–light petroleum, colourless needles of *o*-acetylmethylaminophenol, m. p. 151°, being obtained.

1-*Phenylbenzoxazole Methiodide.*—1-Phenylbenzoxazole, prepared by Skraup's method (*loc. cit.*), was heated (3·8 g.) with methyl iodide (9 g.) at 100° for 36 hours. The product was extracted with dry ether and cautiously crystallised from absolute alcohol. The *methiodide* (yield 4·8 g.) separated in almost colourless needles, m. p. 196° (decomp.), which became brown on exposure to light (Found: C, 49·9; H, 3·6; I, 37·3. $C_{14}H_{12}ONI$ requires C, 49·9; H, 3·6; I, 37·6%).

Action of Water on 1-*Phenylbenzoxazole Methiodide.*—When the salt (3·37 g.) was dissolved in warm water (100 c.c.), a colourless, crystalline substance immediately began to separate. The acid solution on titration with sodium hydroxide and phenolphthalein required 10·4 c.c. of *N*-NaOH (Calc. for 1 equiv. of NaOH, 10·0 c.c.).

The solid crystallised from aqueous alcohol in plates, m. p. 163—164°, and was recognised as *o*-benzoylmethylaminophenol by analysis as well as by the method of preparation. Ransom (*Amer. Chem. J.*, 1900, **23**, 34) gives m. p. 162—163° (Found: C, 74·1; H, 5·6; N, 6·4. Calc., C, 74·0; H, 5·7; N, 6·2%).

The *urethane* was prepared by heating *o*-benzoylmethylaminophenol (1 g.) for 3 hours with phenylcarbimide (0·6 g.). The product was extracted with ether and crystallised from alcohol in colourless plates, m. p. 144° (Found: C, 73·3; H, 5·1; N, 8·2. $C_{21}H_{18}O_3N_2$ requires C, 72·8; H, 5·2; N, 8·1%).

o-*Benzoylmethylaminoanisole.*—*o*-Methylaminoanisole, prepared by the usual reactions from *o*-nitroanisole, was benzoylated with benzoyl chloride and sodium hydroxide. The product crystallised from aqueous alcohol in small, colourless prisms, m. p. 115° (Found: C, 74·4; H, 6·1; N, 5·7. $C_{15}H_{15}O_2N$ requires C, 74·7; H, 6·2; N, 5·8%).

When 1-phenylbenzoxazole methiodide (1·5 g.) was shaken with sodium hydroxide and methyl sulphate in slight excess, a paste formed which was crystallised from aqueous alcohol. It melted at 115°, and did not depress the melting point of *o*-benzoylmethylaminoanisole prepared as described above (Found: N, 5·8%).

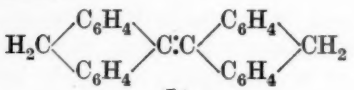
38, Park Road, Hampton Wick. [*Received, August 28th*, 1925.

XXXV.—*Reactions of the* meso-*Hydroxyanthrones.*

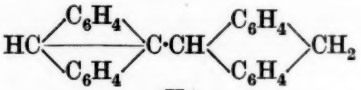
By MARCUS AURELIUS MATTHEWS.

THE reduction of 10-hydroxyanthrone * by zinc dust and glacial acetic acid leads to anthrone, probably through addition of hydrogen to the carbonyl group and subsequent loss of water across the ring (K. H. Meyer, *Annalen*, 1911, **379**, 37).

Anthrone itself on reduction with zinc and hydrochloric acid in glacial acetic acid undergoes the pinacol condensation (Barnett and Matthews, J., 1923, **123**, 380), and it has now been found that under similar conditions 10-hydroxyanthrone also undergoes the pinacol condensation, although the reduction goes further and leads to *dihydrodianthranyl*, which may be (I) or (II) or a tautomeric mixture of these. The powerful blue fluorescence renders (II) the more probable, but the existence of fluorescence cannot be taken as definite proof of the presence of a "bridge" (compare Padova, *Ann. Chim.*, 1910, **19**, 358, 435; Jüngermann, *Ber.*, 1905, **38**, 2868).

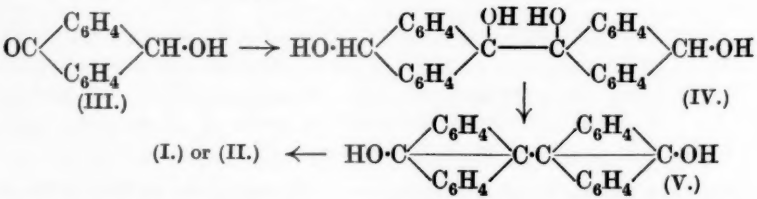


(I.)



(II.)

The reduction of 10-hydroxyanthrone (III) to dihydrodianthranyl cannot take place through preliminary formation of anthrone, for, as already shown (Barnett and Matthews, *loc. cit.*), the reduction of this gives only dianthranyl and α-anthrapinacolin. Further, neither dianthranyl nor dianthranol is attacked under the experimental conditions employed, although dianthranol is reduced to dihydrodianthranyl by tin and hydrochloric acid. It therefore follows that in the reduction of 10-hydroxyanthrone with zinc and hydrochloric acid attack first takes place at the carbonyl group, involving the formation of a pinacol (IV), and that further reduction of the pinacol must be due to ready attack of the "nascent" dianthranol molecule (V) formed by loss of water across the rings.



(III.) (IV.) (I.) or (II.) (V.)

* All the anthrone formulæ given in this paper are numbered with the carbonyl group in position 9.

10-Hydroxy-10-phenylanthrone differs from 10-hydroxyanthrone in giving on reduction a dianthranyl and not a dihydrodianthranyl derivative. Here the mechanism of the reaction probably consists in preliminary reduction to phenylanthrone, from which diphenyldianthranyl is very readily produced (Barnett and Cook, J., 1923, **123**, 2631).

The zinc–hydrochloric acid reduction of the two α-chloro-10-hydroxyanthrones gave compounds for which analytical figures corresponding to the α-chloroanthrones were obtained. The compounds were not the α-chloroanthrones, but each passed into the corresponding α-chloroanthrone on treatment with alcoholic sodium hydroxide. These compounds are at present under investigation and their structure will be discussed in a future communication.

Further information on the mechanism of reduction of a hydroxyanthrone was obtained by comparing the behaviour of 10-hydroxyanthrone itself towards acids and towards reducing agents with that of the two α-chloro-10-hydroxyanthrones :

With	10-Hydroxyanthrone gives	4-Chloro-10-hydroxyanthrone gives	1-Chloro-10-hydroxyanthrone gives
HBr	10-Bromoanthrone	4-Chloro-10-bromoanthrone	1-Chloro-10-bromoanthrone
HCl	10-Chloroanthrone	4 : 10-Dichloroanthrone	1-Chloroanthraquinone and 1-chloroanthrone
HI (1 or 2 mols.)	Anthraquinone and anthrone	1-Chloroanthraquinone and 4-chloroanthrone	4 : 4′-Dichloro-9 : 9′-dianthrone, 1-chloroanthrone, and a trace of 1-chloroanthraquinone
Sn and HCl	Anthrone and a small amount of dihydrodianthranyl	4-Chloroanthrone	4 : 4′-Dichloro-9 : 9′-dianthrone
H_2SO_4	Anthraquinone and anthrone	1-Chloroanthraquinone and 4-chloroanthrone	1-Chloroanthraquinone and 1-chloroanthrone
Al and H_2SO_4	Anthrone	4-Chloroanthrone	1-Chloroanthrone.

10-*Chloroanthrone* is an extremely stable substance and is readily prepared in good yield by the direct chlorination of anthrone, although Goldmann (*Ber.*, 1887, **20**, 2436; 1888, **21**, 1176) failed to obtain it by this method. It is best identified in the form of the *pyridinium* salt, $OH{\cdot}C\langle{}^{C_6H_4}_{C_6H_4}\rangle C{\cdot}C_5H_5NCl$ (VI) or

$$OC\langle{}^{C_6H_4}_{C_6H_4}\rangle CH{\cdot}C_5H_5NCl \quad \text{(VII)}.$$

The direct chlorination of 4-chloroanthrone gave 4 : 10-dichloro-

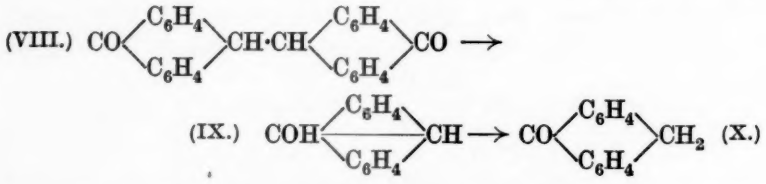
anthrone, whereas from 1-chloroanthrone the only product obtained was 4 : 4′-dichloro-9 : 9′-dianthrone, the 1 : 10-dichloroanthrone apparently being very unstable. It was not possible to prepare the last compound by the action of hydrogen chloride on the corresponding hydroxyanthrone, a disproportioning taking place with the production of the corresponding anthraquinone and anthrone. Other acids cause a disproportioning of the hydroxyanthrones, the mechanism of which has been discussed by Scholl (*Ber.*, 1923, **56**, 1065).

Hydroxyanthrone is readily converted into anthraquinol by boiling water in absence of air, this being the best method for preparing anthraquinol.

Nitration of dihydrodianthranyl leads to a *nitrodihydrodianthranyl*, a reaction which favours formula (II) without, however, excluding formula (I). The nitration is not preceded by oxidation as in the case of dihydroanthracene (Meisenheimer, *Annalen*, 1902, **323**, 205; 1904, **330**, 133), or of dichlorodihydrodianthranyl (Barnett and Matthews, J., 1923, **123**, 2549), the product isolated in the latter case being dichlorodinitrodianthranyl.

Dihydrodianthranyl reacts slowly with excess of bromine in carbon disulphide solution with the production of *dibromodihydrodianthranyl*.

Dianthranol is converted by hydriodic acid in glacial acetic acid exclusively into anthrone and by tin and hydrochloric acid into a mixture of anthrone and dihydrodianthranyl. In these reactions it is improbable that anthrone is produced by the direct reduction of dianthranol and it seems almost certain that reduction is preceded by ketonisation to dianthrone, which is then reduced to anthrone. The suggestion was at first put forward (Barnett and Matthews, J., 1923, **123**, 380) that the reduction of dianthrone (VIII) to anthrone (X) was due to the instability of the dianthranyl ring system, reduction taking place at the bond joining the two *meso*-carbon atoms. Further work has rendered this view improbable, for if the single bond which joins the two anthracene ring systems in dianthrone shows this lack of stability, the corresponding double



bond in dianthraquinone should be even more susceptible to reduction. This, however, is not the case, dianthraquinone on reduction

giving dianthranol and not dianthrone. It therefore seems probable that hydrogen adds on to the carbonyl groups in dianthrone instead of to the single bond joining the two anthracene ring systems. In order to satisfy the requisite valencies, the " bridge " bond must be established with necessary rupture of the bond joining the two anthracene ring systems; the anthranol thus produced being at once ketonised to anthrone (X).

A similar explanation suffices to account for the reduction of 4 : 4′-dichloro-9 : 9′-dianthrone to the corresponding anthrone.

EXPERIMENTAL.

Dihydrodianthranyl (I or II).—To 20 g. of 10-hydroxyanthrone in 100 c.c. of boiling glacial acetic acid, 20 g. of zinc dust and 50 c.c. of concentrated hydrochloric acid were added simultaneously in small amounts. The addition of these two reagents must be simultaneous, since excess of hydrochloric acid causes decomposition of the hydroxyanthrone and excess of zinc dust brings about reduction to anthrone (Meyer, *loc. cit.*). After refluxing for 5 minutes the solid was separated from the hot solution. It crystallised from pyridine as an additive compound in greenish-yellow, flat needles, which lost pyridine on drying in the steam-oven for 3 days. The product (6 g.) became yellowish-grey and melted at 298—300° to a black liquid. In this state, it is pure enough for most purposes. For analysis it was recrystallised four times from benzene (Found : C, 94·5; H, 5·7. $C_{28}H_{20}$ requires C, 94·4; H, 5·6%).

Dihydrodianthranyl exhibits an intense violet-blue fluorescence in organic solvents. It is easily soluble in chloroform, but less so in carbon disulphide, pyridine, acetone, or ether.

Dibromodihydrodianthranyl.—Excess of bromine (1 c.c.) was added to a cold solution of dihydrodianthranyl in carbon disulphide. After 12 hours, most of the carbon disulphide was distilled off, ether added, and the resulting solid recrystallised twice from small quantities of pyridine and dried in the steam-oven (Found : C, 65·4; H, 3·6; Br, 31·1. $C_{28}H_{18}Br_2$ requires C, 65·4; H, 3·5; Br, 31·1%).

Dibromodihydrodianthranyl forms yellow crystals which do not melt at 320° and darken on exposure to light. Its solutions exhibit a blue fluorescence.

Nitrodihydrodianthranyl.—Excess of nitric acid (*d* 1·42; 2 c.c.) was added to 1·5 g. of finely powdered dihydrodianthranyl suspended in 50 c.c. of cold glacial acetic acid. After 12 hours, the solid was collected, washed with acetic acid, and dried in the steam-oven. The same compound was also obtained when the nitration was carried out at 80—100° and only one molecule of nitric acid

used. For analysis, it was recrystallised twice from glacial acetic acid, in which it was very sparingly soluble, separating in golden-yellow needles which melted and decomposed at 305° and darkened on exposure to light (Found: C, 83·6; H, 4·9. $C_{28}H_{19}O_2N$ requires C, 83·8; H, 4·7%).

Dichlorodinitrodianthranyl.—Dichlorodihydrodianthranyl * (Barnett and Matthews, J., 1923, **123**, 2549) in cold glacial acetic acid suspension was resistant to nitric acid, but oxidation and nitration took place when 3 g. of the finely powdered material were suspended in 30 c.c. of glacial acetic acid, 2 c.c. of nitric acid (*d* 1·42) added, and the whole slowly heated to the b. p. After cooling, the orange-red solid was collected, washed with acetic acid and ether, and recrystallised twice from small quantities of pyridine–alcohol. It then formed orange-red needles which became dark red on exposure to light and did not melt at 330° (Found: C, 65·5; H, 3·5; Cl, 13·8. $C_{28}H_{14}O_4N_2Cl_2$ requires C, 65·5; H, 2·7; Cl, 13·8%).

Reduction of 10-*Hydroxy*-10-*phenylanthrone.*—To 2·3 g. of hydroxyphenylanthrone and 25 c.c. of boiling glacial acetic acid, 2 g. of zinc dust and 4 c.c. of concentrated hydrochloric acid were added simultaneously, and the whole was boiled under reflux for 5 minutes. After cooling, the solid was collected and the excess of zinc removed by digestion with dilute hydrochloric acid. The resulting diphenyldianthranyl (1·5 g.) was identified by analysis (C, 94·9; H, 5·2. Calc., C, 94·9; H, 5·1%) and by direct comparison with an authentic sample.

Reduction of Dianthranol.—(*a*) To 3 g. of dianthranol and 5 g. of zinc dust in 40 c.c. of boiling glacial acetic acid, 8 c.c. of concentrated hydrochloric acid were added during 2½ hours, and the boiling was continued for a further ½ hour. The yellow solid which separated from the filtered solution on cooling consisted mainly of unchanged dianthranol.

(*b*) Finely powdered dianthranol (3 g.) and zinc dust (12 g.) were heated on the water-bath with 50 c.c. of ammonia (*d* 0·880) and 50 c.c. of water for 3 days with occasional additions of more ammonia, sodium hydroxide, and zinc dust. The hot solution was filtered, the zinc dust extracted with dilute hydrochloric acid, and the residue recrystallised from pyridine; 0·6 g. of anthracene (m. p. 217°) was thus obtained.

(*c*) Dianthranol (1 g.) was boiled under reflux for 5 minutes with 20 c.c. of glacial acetic acid and 2 c.c. (2 mols.) of hydriodic acid (*d* 1·7), and the whole then diluted with hot water to incipient crystallisation. The dark crystals which separated on cooling were

* The m. p. of this compound, owing to a misprint, was given in the paper cited as 288° instead of 268°.

boiled with potassium iodide solution, and 0·9 g. of anthrone obtained. Dianthrone under similar conditions also gave anthrone.

(*d*) Dianthranol (5 g.), tin (8 g.), and glacial acetic acid (80 c.c.) were boiled under reflux and concentrated hydrochloric acid (15 c.c.) was added during 1 hour. After boiling for a further ½ hour, the hot solution was filtered. The dihydrodianthranyl which separated on cooling was recrystallised from benzene (yield 0·8 g.). The acetic liquors on dilution with water gave anthrone, which was recrystallised from glacial acetic acid and converted into anthranyl acetate.

The products in (*b*), (*c*), and (*d*) were each identified by comparison with an authentic specimen.

Reduction of Dianthraquinone.—Dianthraquinone (0·5 g.) and zinc dust (2 g.) were suspended in boiling glacial acetic acid (10 c.c.), and concentrated hydrochloric acid (3 c.c.) was added during 20 minutes. After filtration, dilute hydrochloric acid was added and the solid recrystallised from acetone. It was identified as dianthranol by its complete solubility in cold aqueous sodium hydroxide and by the preparation of dianthranyl diacetate.

1-*Chloro*-9-*anthranyl Acetate.*—A mixture of 5 g. of 1-chloro-9-anthrone, 30 c.c. of pyridine, and 7 c.c. of acetic anhydride was heated on the boiling water-bath for 15 minutes and then poured into boiling water. The solid after recrystallisation from alcohol formed long, yellow needles, m. p. 110—112° (yield 4·8 g.). Its alcoholic solutions exhibit a blue fluorescence (Found: Cl, 13·2. $C_{16}H_{11}O_2Cl$ requires Cl, 13·1%).

4-*Chloro*-9-*anthranyl Acetate.*—A similar mixture containing 4-chloro-9-anthrone * was heated for 10 minutes, the subsequent procedure being as above. The product formed almost colourless needles, m. p. 124—126° (yield 4·6 g.) (Found: Cl, 13·2%). Its solution in alcohol had a blue fluorescence.

1-*Chloro*-10-*bromoanthrone.*—Bromine (4 c.c.; 1 mol.) was added to 18 g. of finely powdered 1-chloroanthrone suspended in 50 c.c. of carbon disulphide. The solid (22·5 g.), after being washed with carbon disulphide and ether, was pure enough for most purposes, but for analysis a sample was recrystallised twice from chloroform, in which it was moderately soluble, separating in faintly yellow crystals, m. p. 165° (decomp.), which darkened on exposure to light (Found: Cl + Br, 37·75. $C_{14}H_8OClBr$ requires Cl + Br, 37·6%).

1-*Chloro*-10-*hydroxyanthrone.*—The above bromo-compound (22 g.) was boiled under reflux with 240 c.c. of acetone and 160 c.c. of water

* In preparing this compound by Barnett and Matthews's method (J., 1923, **123**, 2549) the reduction must not be too prolonged, since it has been found that 4-chloro-9-anthrone—unlike anthrone itself—slowly undergoes the pinacol condensation with tin and hydrochloric acid with the production of dichlorodihydrodianthranyl.

until an almost clear solution was obtained (about 5 minutes), the filtered solution was cooled in ice, and 160 c.c. of water were added slowly.* The resulting solid was recrystallised three times from benzene and then formed fine, white needles, m. p. 144—145°, which dissolved in boiling aqueous sodium hydroxide to form a deep red solution (Found: Cl, 14·6. $C_{14}H_9O_2Cl$ requires Cl, 14·5%).

4-Chloro-10-hydroxyanthrone.—4-Chloro-10-bromoanthrone (5 g.) was refluxed with 120 c.c. of acetone and 80 c.c. of water for 15 minutes, the filtered solution cooled in ice, and cautiously diluted with 100 c.c. of water. The yellow solid (2·5 g.) was washed with water, dried in a vacuum desiccator, and twice recrystallised from benzene; it then formed faintly yellow crystals, m. p. 144—145°. It is not altered in m. p. by mixing with 1-chloro-10-hydroxyanthrone (Found: Cl, 14·5%).

10-Chloroanthrone.—(*a*) Dry hydrogen chloride was passed for 10 minutes through a suspension of 5 g. of finely powdered 10-hydroxyanthrone in 40 c.c. of toluene, a yellow precipitate forming. After dilution with light petroleum, the solid was collected and recrystallised from benzene, from which it separated with benzene of crystallisation, which was lost on drying in the steam-oven (Found: Cl, 15·5. $C_{14}H_9OCl$ requires Cl, 15·5%).

10-Chloroanthrone forms colourless needles which melt and evolve gas at 225°. It is very much more stable than the corresponding bromo-compound and can be recrystallised from boiling xylene. It is stable towards boiling dilute solutions of alkali hydroxides, but dissolves in their alcoholic solution with a yellow colour. It is hydrolysed, but very much more slowly than 10-bromoanthrone, to 10-hydroxyanthrone by boiling with aqueous acetone.

(*b*) Finely powdered 10-hydroxyanthrone (1 g.) was boiled with 50 c.c. of concentrated hydrochloric acid for ½ hour. The product was recrystallised from xylene and identified by its conversion into anthronylpyridinium chloride (see below).

(*c*) Very finely powdered anthrone (40 g.) was added to 180 c.c. of a solution of chlorine in carbon tetrachloride (9·5% weight-volume). The reaction was extremely sluggish, but took place rapidly with evolution of heat on the addition of a trace of iodine, so that cooling with water became necessary. When it was complete (about 10 minutes) the whole was cooled in ice, and the solid, after being washed with carbon tetrachloride and ether, was dried in the steam-oven. The yield was 33 g. and the product pure enough for most purposes without further treatment. It was identified by its conversion into anthronylpyridinium chloride.

* In this and the succeeding preparation the addition of water must be made cautiously, otherwise the product separates as an oil.

10-*Hydroxyanthranyl*-9-*pyridinium Chloride* (VI) *or Anthronyl-pyridinium Chloride* (VII).—Chloroanthrone (2 g.) was heated with 15 c.c. of pyridine on the water-bath for 15 minutes, the crystals were washed with ether and then twice recrystallised from very dilute hydrochloric acid; orange-red needles, m. p. 204° (decomp.), were obtained (Found: Cl, 11·0. $C_{19}H_{14}ONCl,H_2O$ requires Cl, 10·9%).

This chloride is easily identified by its reactions, which are similar to those of the corresponding bromide (Barnett, Cook, and Grainger, J., 1922, **121**, 2059).

4 : 10-*Dichloroanthrone.*—(*a*) Dry hydrogen chloride was passed for 10 minutes through 3 g. of finely powdered 4-chloro-10-hydroxyanthrone suspended in 20 c.c. of benzene; the solid slowly dissolved and crystals began to separate. After addition of light petroleum, these were collected and twice recrystallised from small quantities of chloroform and light petroleum, faintly yellow crystals being obtained, m. p. 127—128° (Found: Cl, 26·9. $C_{14}H_8OCl_2$ requires Cl, 27·0%).

1-Chloro-10-hydroxyanthrone, when treated with hydrogen chloride under identical conditions, gave a mixture of 1-chloroanthraquinone and 1-chloro-9-anthrone.

(*b*) A solution of chlorine in carbon tetrachloride (10 c.c.; 9·5% weight-volume) was added to finely powdered 4-chloro-9-anthrone (3 g.) suspended in 10 c.c. of carbon tetrachloride. No reaction took place until a crystal of iodine was added; hydrogen chloride was then slowly evolved and the solid dissolved. After concentration to small bulk, light petroleum was added and the solid recrystallised from a small quantity of chloroform–light petroleum. It was identified as 4 : 10-dichloroanthrone by the method of mixed melting points.

1-Chloro-9-anthrone, when treated under identical conditions, gave 4 : 4′-dichloro-9 : 9′-dianthrone as the sole product.

Anthraquinol.—Finely powdered 10-hydroxyanthrone (3 g.) was boiled with 100 c.c. of air-free water in an atmosphere of carbon dioxide for 20 minutes. The precipitate was identified as anthraquinol by its complete solubility in cold aqueous sodium hydroxide, by its facile oxidation to anthraquinone, and by the preparation of anthraquinyl diacetate. If the boiling with water is continued for a longer time, the product will be contaminated with some anthraquinone.

The action of acids and reducing agents on 10-hydroxyanthrone and on the two α-chlorohydroxyanthrones, the results of which are given in the theoretical part of this paper, were carried out as follows:

Hydrobromic acid. The conditions were similar to those already described in the case of hydrochloric acid.

Hydriodic acid. The hydroxyanthrone (1 g.) was dissolved in boiling glacial acetic acid (10 c.c.), 1 or 2 mols. of hydriodic acid (*d* 1·7) were added, the whole was boiled for 1 minute in an atmosphere of carbon dioxide, and the solution then diluted with water.

Tin and hydrochloric acid. The hydroxyanthrone (1 g.), glacial acetic acid (10 c.c.), and tin (2 g.) were boiled under reflux, and concentrated hydrochloric acid (2 c.c.) was added during 5 minutes. The dianthrone or dihydrodianthranyl was filtered from the boiling solution. The filtrate on cooling deposited the anthrone.

Sulphuric acid. The hydroxyanthrone was dissolved in a small quantity of concentrated sulphuric acid in an atmosphere of carbon dioxide, kept in the cold for 15 minutes, and the product precipitated by pouring into ice-water.

Aluminium and sulphuric acid. The hydroxyanthrone (1 g.) was dissolved in concentrated sulphuric acid (11 c.c.), and aluminium powder (0·25 g.) added with cooling. A series of colour changes took place, the end of the reaction being determined by frothing and by the changing of the dark colour of the solution to light yellow or green (about $\frac{3}{4}$ hour). The product was precipitated by pouring into ice-water and purified by recrystallisation.

The identification of the compounds formed in the above reactions was effected usually by means of direct comparison with authentic samples. 1-Chloro- and 4-chloro-9-anthrone were differentiated by the preparation of the respective anthranyl acetates. When an anthrone occurred together with an anthraquinone, separation was not practicable by means of fractional crystallisation. The anthraquinone was detected by the anthraquinol test. The anthrone was detected by dissolving some of the mixture in boiling alcoholic sodium hydroxide and adding a drop of chloroform: if anthrone is present, a green colour is produced (compare Padova, *Compt. rend.*, 1909, **148**, 290); if 1-chloro-9-anthrone is present, a green colour will also develop; but if 4-chloro-9-anthrone is present, a dirty brown colour appears, thus affording a means of differentiating between 1- and 4-chloroanthrones. The most effective way of identifying 4 : 4′-dichloro-9 : 9′-dianthrone was by reducing 0·5 g. with tin (1 g.) in boiling glacial acetic acid (40 c.c.) and adding concentrated hydrochloric acid (3 c.c.) until all the solid matter had gone into solution (1½ hours). After filtration from the undissolved tin, water was added to incipient crystallisation, and the 1-chloro-9-anthrone thus obtained identified by direct comparison with an authentic sample.

Summary.

1. The reduction of 10-hydroxyanthrone and 10-hydroxy-10-phenylanthrone has been studied. Both compounds undergo the pinacol condensation with the production of dihydrodianthranyl and diphenyldianthranyl respectively.

2. The reduction of dianthranol under various conditions has been found to give anthracene, anthrone, and dihydrodianthranyl.

3. The mechanism of the reduction of a dianthrone to an anthrone has been discussed.

4. 10-Chloroanthrone, a substance of remarkable stability, has been prepared by the action of hydrochloric acid on 10-hydroxyanthrone and of chlorine on anthrone.

5. The action of acids and reducing agents on hydroxyanthrone and 1- and 4-chloro-10-hydroxy-9-anthrones has been examined. With some acids a disproportioning to the corresponding anthraquinone and anthrone takes place; reduction usually leads to the corresponding anthrone.

6. Hydroxyanthrone is easily enolised to anthraquinol by boiling water.

The author desires to express his thanks to the Department of Scientific and Industrial Research for a grant which enabled him to carry out this work.

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JEWRY STREET, E.C. 3. [*Received, September* 14*th*, 1925.]

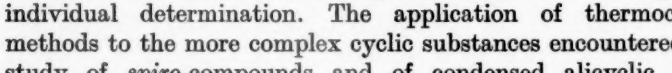
XXXVI.—cyclo*Hexane*spirocyclo*hexane*.

By WOODFORD STANLEY GOWAN PLUCKNETT NORRIS.

THERE is remarkable agreement between the relative ease of production of homologous alicyclic rings, the "formation numbers" calculated from the interatomic angle (115°) in saturated carbon chains (Ingold, J., 1921, **119**, 305), and the heats of ring formation (Stohmann and Kleber, *J. pr. Chem.*, 1892, **45**, 475). The effect of substitution (particularly substitution of a *gem*-grouping) on the ease of closure in any of the simple *cyclo*paraffins is very pronounced, even in comparison with the difference, in ease of ring formation, between one member of the series and the next. If, therefore, the above agreement is fundamental and not fortuitous, the introduction of a substituent should cause an alteration in the heat of formation of a *cyclo*paraffin ring comparable with the differences, in heat of formation, between successive ring homologues; indeed,

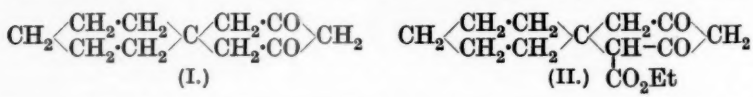
the alteration should be much greater than the accuracy of any individual determination. The application of thermochemical methods to the more complex cyclic substances encountered in the study of *spiro*-compounds and of condensed alicyclic systems should therefore be capable of giving an actual quantitative measure of the influence of substituents on ease of ring formation.

It would, for example, be possible, by determining the heats of combustion of two corresponding series of hydrocarbons (A) and (B), in which R and R′ are progressively altered, to obtain a measure



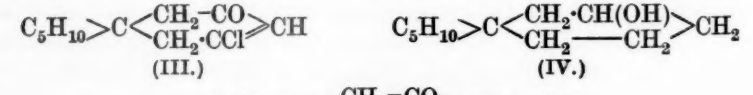
of the effect of substitution on the ease of closure of the ring present in (B). The chief interest of such a line of work would lie in the spirocyclic series. Spiran hydrocarbons have not, however, hitherto been described.* One such hydrocarbon, cyclo*hexane*-spirocyclo*hexane*, has now been prepared.

An account of the initial stages of the synthesis has already appeared (Norris and Thorpe, J., 1921, **119**, 1199). *cyclo*Hexane-*spirocyclo*hexane-3 : 5-dione (I) was obtained by hydrolysing the ester (II); the latter was prepared by the condensation of Wallach's ketone, *cyclo*hexylideneacetone, $C_5H_{10}{>}C{:}CH{\cdot}COMe$, with ethyl sodiomalonate. The reduction of the diketone (I) has now been



accomplished by indirect methods similar in general to those by which Crossley and Renouf (J., 1905, **87**, 1494; 1907, **91**, 63) prepared 1 : 1-dimethyl*cyclo*hexane.

Crossley and Le Sueur (J., 1903, **83**, 110) found that dimethyldihydroresorcinol was converted into 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one by means of phosphorus trichloride in chloroform



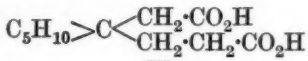
solution. The *spiro*-diketone (I) similarly gives the unsaturated *chloro-ketone* (III). Reduction of this with sodium and moist ether

* Ingold (J., 1923, **123**, 1706) has shown conclusively that the hydrocarbon hitherto represented to be *cyclo*propane*spirocyclo*propane consists essentially of methyl*cyclo*butene, unaccompanied by any of its isomerides in the *cyclo*propane series.

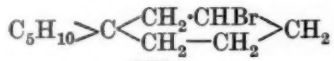
(compare Crossley and Renouf, *loc. cit.*) produced much resinous matter, from which only a trace of the *spiro*-alcohol (IV) could be isolated. However, by the action of zinc dust on the chloro-ketone in boiling glacial acetic acid solution, cyclo*hexane*spirocyclo*hexan*-3-*one* (V), which is analogous to Kon's *cyclo*hexane*spirocyclo*butan-3-one (J., 1922, **121**, 515), was obtained in reasonable yield.

The refractive power of the ketone (V) was measured for sodium light and for the red and blue hydrogen lines, but not for the violet line on account of selective absorption. The molecular refraction shows inappreciable exaltation (0·08), in contrast with the increase (0·77) observed by Kon in the molecular refraction of his ketone; moreover, the molecular dispersion between the red and the blue shows no increase over the theoretical value. This result will not be surprising when it is remembered that *cyclo*pentanes and *cyclo*hexanes normally show scarcely any optical anomaly (compare Eisenlohr, " Spektrochemie organischer Verbindungen "), and that the figure of instability * (maximum valency curvature) for *cyclo*hexane*spirocyclo*hexane is only 0·22, as against 0·18 for 1 : 1-dimethyl*cyclo*hexane, 0·08 for *cyclo*hexane itself, and 0·13 for *cyclo*pentane.

The ketone (V) gave, on reduction with sodium and moist ether, a good yield of cyclo*hexane*spirocyclo*hexan*-3-*ol* (IV). The constitution of this alcohol was confirmed by oxidising it with nitric acid to *cyclo*hexane-1-acetic-1-propionic acid (VI).

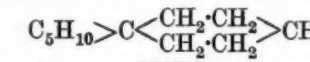


(VI.)

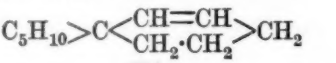


(VII.)

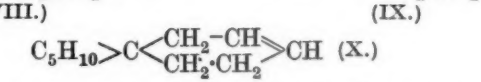
The conversion of the *spiro*-alcohol (IV) into the *bromo*-derivative (VII) by the action of fuming hydrobromic acid presented unexpected difficulties. Not only did the replacement of the hydroxyl group by bromine proceed with great reluctance, but the boiling points of the two compounds lie very close together, rendering even partial separation a very tedious process. The same difficulty was encountered in attempts to isolate the corresponding *chloro*-derivative.



(VIII.)



(IX.)



(X.)

By reducing the impure bromo-compound (VII) in alcohol with zinc dust, *cyclo*hexane*spirocyclo*hexane (VIII) was obtained together

* The figure of instability for a 6-carbon ring is expressed by

$$[\delta\alpha/\delta S]_{\theta=\theta} = \sin\theta - \sqrt{3}.\cos\theta.$$

with an unsaturated hydrocarbon (IX or X), evidently produced by loss of hydrogen bromide; a result contrasting with the production under similar conditions of 1 : 1-dimethyl*cyclo*hexane only from 3-bromo-1 : 1-dimethyl*cyclo*hexane (Crossley and Renouf, *loc. cit.*).

The final stage in the reduction was effected by shaking the mixture of saturated and unsaturated hydrocarbons with colloidal palladium in an atmosphere of hydrogen.

This investigation cannot be continued for the present, but it will, it is hoped, be concluded at some future date.

EXPERIMENTAL.

cyclo*Hexane*spirocyclo*hexan*-3 : 5-*dione* (I).—The diketone of Norris and Thorpe (*loc. cit.*) has been further characterised by the formation, on hydrolytic fission, of cyclo*hexane*-1-*acetone*-1-*acetic acid*, $C_5H_{10}{>}C{<}\begin{matrix}CH_2\cdot COMe\\CH_2\cdot CO_2H\end{matrix}$. The diketone (1 g.) and 6 g. of crystalline barium hydroxide dissolved in 25 c.c. of water were heated at 200° for 24 hours. The ethereal extract of the acidified liquid left, after evaporation of the solvent, a pale yellow oil (yield practically quantitative), which set on cooling to a white solid and gave no colour with ferric chloride. The *keto-acid*, which is volatile in steam, is very soluble in ether, benzene, or alcohol, less so in water, or light petroleum (b. p. 40—60°); it separates from the latter in short, colourless needles, m. p. 67° (Found: C, 66·8; H, 8·8. $C_{11}H_{18}O_3$ requires C, 66·7; H, 9·1%). The *semicarbazone* separates from methyl alcohol in colourless plates, m. p. 183·5° (decomp.) (Found: C, 56·55; H, 8·4; N, 16·6. $C_{12}H_{21}ON_3$ requires C, 56·4; H, 8·3; N, 16·5%).

Action of Phosphorus Trichloride on the Diketone (I). cyclo*Hexane*spiro-5-*chloro*-Δ^4-cyclo*hexen*-3-*one* (III).—A mixture of 67 g. of the diketone (which must be dry and free from resinous matter and hydrochloric acid), 250 c.c. of dry chloroform, and 17·5 g. of phosphorus trichloride was heated under reflux for 3 hours, cooled, and the unchanged diketone filtered off. The residue after distillation of the chloroform was dissolved in a little ether and poured into 1300 c.c. of water, which was then extracted with ether four times. The ethereal solution, after being thoroughly washed with 10% sodium hydroxide solution (from which more of the diketone was obtained on acidification), was washed once with 25% sulphuric acid, twice with water, and dried over calcium chloride. The residue, after the ether had been removed through a column, was distilled under reduced pressure. The *chloro-ketone*, b. p. 167°/30 mm., 160°/17 mm., 157°/12 mm., solidified, on cooling, to a white, crystalline mass, which had a pungent camphor-like odour and

separated from light petroleum (b. p. 60—80°) in large, colourless prisms, m. p. 47° (Found : Cl, 17·8. $C_{11}H_{15}OCl$ requires Cl, 17·8%).

The *semicarbazone* separates from methyl alcohol in glistening plates, m. p. 219° (decomp.) (Found : N, 17·0, 16·2. $C_{12}H_{18}ON_3Cl$ requires N, 16·4%).

The recovered diketone (24%) was purified with difficulty, owing to the presence of resinous phosphorus compounds, and in many cases could not be used again.

Reduction of the Chloro-ketone with Zinc Dust in Glacial Acetic Acid. cyclo*Hexane*spirocyclo*hexan*-3-*one* (V).—Zinc dust (33 g.) was added, the first portions in very small quantities because of the violence of the reaction, during 24 hours to a solution of 25 g. of the chloro-ketone in 80 c.c. of glacial acetic acid, boiling under reflux. The liquid was neutralised with caustic soda solution and steam-distilled. From the distillate, ether extracted the ketone (yield 86%).

The *semicarbazone* separated from ethyl alcohol in colourless, flattened needles, m. p. 224·5° (decomp.) (Found : N, 18·9. $C_{12}H_{21}ON_3$ requires N, 18·8%).

The *ketone*, regenerated from the semicarbazone by boiling with oxalic acid and water in a current of steam, and extracted from the distillate with ether, was a colourless, mobile liquid, b. p. 225°/772 mm. or 130°/15 mm., having a pungent odour similar to that of cedarwood oil (Found : C, 79·8; H, 10·7. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%). The freshly distilled ketone had $d^{21·7}$ 0·98417, n_C 1·48432, $n_D = 1·48685$, n_F 1·49322 (no violet light was transmitted). Hence $[R_L]_D = 48·55$; $[R_L]_{F-C} = 0·76$, the calculated values being 48·61 and 0·75, respectively.

The ketone is stable towards neutral permanganate, and slowly attacked by the alkaline reagent in the cold.

The *oxime*, prepared by boiling the ketone for 1 hour with hydroxylamine hydrate (1·5 mols.) in aqueous-alcoholic solution, separated from light petroleum (b. p. 40—80°) in large, colourless prisms, m. p. 128° (Found : C, 73·1; H, 10·6. $C_{11}H_{19}ON$ requires C, 72·9; H, 10·6%).

Reduction of the spiro*Ketone with Sodium in Moist Ether.* cyclo-*Hexane*spirocyclo*hexan*-3-*ol* (IV).—A solution of 18 g. of the crude ketone (from the reduction of 25 g. of chloro-ketone) in 100 c.c. of ether and 10 c.c. of alcohol was poured on to 200 c.c. of water in a separating funnel, to which was attached a reflux condenser. Sodium (19 g., in thin slices) was gradually added, the water being changed after addition of the first 10 g.; this water was extracted with a little ether, which was then transferred to the funnel. When all the sodium had been added, the ethereal solution was washed

twice with water, the ether removed through a column, and the residue distilled in steam. The ethereal extract of the distillate was washed twice with a saturated solution of sodium bisulphite, and the ether distilled through a column; the residue solidified on cooling in a vacuum (yield 50% of the theoretical, calculated on the chloro-ketone used).

cyclo*Hexane*spirocyclo*hexan*-3-*ol* boils at 127—128°/15 mm. and sets to a felted mass of needles, which are too soluble in the ordinary solvents to be recrystallised, but melt quite sharply at 58° after draining well on porous porcelain (Found: C, 78·5; H, 11·75. $C_{11}H_{20}O$ requires C, 78·5; H, 12·0%). The alcohol has a pleasant camphoraceous odour.

The p-*nitrobenzoate* is produced when the hydroxy-compound and *p*-nitrobenzoyl chloride are boiled with pyridine in ethereal solution. It separates from alcohol in pearly-white plates, m. p. 102° (Found: C, 68·3; H, 7·25. $C_{18}H_{23}O_4N$ requires C, 68·1; H, 7·3%).

Oxidation of the spiro*Alcohol.* cyclo*Hexane*-1-*acetic*-1-*propionic Acid* (VI).—The hydroxy-compound (19 g.) was gradually added to 45 c.c. of boiling, concentrated nitric acid, and the liquid was then diluted with water and evaporated. This process was repeated until no more nitric acid remained. A gummy acid (19·5 g.) was thus obtained (compare Crossley and Renouf, *loc. cit.*) which did not solidify. This was kept for 36 hours with 60 c.c. of absolute alcohol and 20 c.c. of concentrated sulphuric acid. The fraction, b. p. 179—183°/14 mm., of the neutral ester thus produced (Found: C, 66·4; H, 9·5. $C_{15}H_{26}O_4$ requires C, 66·6; H, 9·7%) was hydrolysed with boiling alcoholic caustic potash, and the acid extracted from the acidified solution with ether. The residue left after evaporation of the ether gradually solidified when kept in a vacuum, and, after remaining for 3 days in contact with porous porcelain, was recrystallised from a mixture of chloroform and light petroleum (b. p. 40—60°), from which it separated in rosettes of colourless needles, m. p. 142·5° (Found: C, 61·45; H, 8·4. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·4%).

The acid may also be purified through the characteristic *calcium* salt, the solubility of which in water apparently increases with increasing temperature almost to the boiling point, and then suddenly decreases.

Action of Hydrobromic Acid on the Hydroxy-compound.—The *spiro*-alcohol (20 g.) was heated for 1·5 hours in a sealed soda-water bottle with 110 c.c. of fuming hydrobromic acid, saturated at 0°. The cooled liquid was resaturated with hydrogen bromide, and the

heating repeated. The product was poured into 1500 c.c. of water, and the heavy oil extracted with ether. The ethereal solution was washed well with a solution of sodium carbonate and then with water, and dried over calcium chloride. The residue, after the ether had been removed through a column, was distilled under reduced pressure. The greater portion boiled between 133° and 136°/12 mm., but the liquid could not be separated into definite fractions, even by repeated distillation. A portion taken at 133° gave the following figures on analysis : C, 61·2; H, 8·7; Br, 29·2. $C_{11}H_{19}Br$ requires C, 57·1; H, 8·3; Br, 34·6%. These correspond to 84% of the bromo-derivative, if only bromo-compound and hydroxy-compound were present. A purer sample was not obtained.

Action of Hydrochloric Acid on the Hydroxy-compound.—The reaction was conducted as in the preceding case. The fraction of the product most rich in chlorine boiled at 142—148°/33 mm. and contained 13·7% of chlorine, corresponding with the presence of 72% of $C_{11}H_{19}Cl$ in the mixture. No fraction containing more than this amount of chlorine could be isolated.

Reduction of the Bromo-derivative (VII) *with Zinc Dust and Alcohol.*—The crude bromo-compound (26·5 g.), containing 84% of the pure material, was dissolved in 90 c.c. of 90% alcohol and mixed with 46 g. of zinc dust and an equal bulk of sand. Enough absolute alcohol (*ca.* 10 c.c.) was added to form a clear solution, and the whole heated under reflux on the water-bath for 20 hours. The liquid was filtered into 1200 c.c. of water, and the aqueous liquid extracted twice with ether. The ethereal solution was washed with water, and dried over potassium carbonate, the ether removed, and the residue heated for 2 hours over metallic sodium and then distilled. After two further distillations over sodium (the third time the metal remained unattacked), a bright, colourless liquid, b. p. 204—208°/762 mm., was obtained having a penetrating odour of geranium (Found in a fraction, b. p. 204—206° : C, 87·4; H, 13·0. Found in a fraction, b. p. 206—208° : C, 87·35; H, 12·9. $C_{11}H_{20}$ requires C, 86·8; H, 13·2%. $C_{11}H_{18}$ requires C, 88·0; H, 12·0%. A 50% mixture of $C_{11}H_{20}$ and $C_{11}H_{18}$ requires C, 87·4; H, 12·6%).

These figures indicate that the hydrocarbon contained some unsaturated material, a conclusion which was confirmed by the ready absorption of bromine in chloroform solution and by the reduction of permanganate in acetone solution. The analytical figures are so close to those given above for a 50% mixture that at first it was thought that a reaction in the following sense must have occurred :

$$2C_5H_{10}{>}C{<}\begin{matrix}CH_2{\cdot}CHBr\\CH_2{-}CH_2\end{matrix}{>}CH_2 + Zn \longrightarrow ZnBr_2 +$$

$$C_5H_{10}{>}C{<}\begin{matrix}CH_2{-}CH\\CH_2{\cdot}CH_2\end{matrix}{>}CH_2\ CH_2{<}\begin{matrix}CH{-}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}C{<}C_5H_{10}\quad (C_{22}H_{38})$$

followed by isomeric change on distillation :

$$C_{22}H_{38} \longrightarrow \underset{(C_{11}H_{20})}{C_5H_{10}{>}C{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}CH_2} + \underset{(C_{11}H_{18})}{C_5H_{10}{>}C{<}\begin{matrix}CH_2{-}CH\\CH_2{\cdot}CH_2\end{matrix}{>}CH}$$

These figures have, however, never been repeated; moreover, 3 g. of the hydrocarbon mixture absorbed, in chloroform solution, 0·345 g. of bromine only, whereas for a 50% mixture 0·530 g. should have been taken up. It is concluded, therefore, that the remarkable agreement of the analytical results with the numbers required for the composition "$C_{22}H_{38}$" is accidental, and that reduction and elimination of hydrogen bromide must have occurred simultaneously.

Reduction of the Hydrocarbon Mixture with Hydrogen and Colloidal Palladium. cyclo*Hexane*spirocyclo*hexane* (VIII).—The mixed hydrocarbons (6 g.) were shaken in an atmosphere of hydrogen for 8 hours with 2·5 c.c. of a 10% solution of palladium chloride, 2·5 c.c. of a 10% solution of gum arabic in water, 5 c.c. of water, and enough alcohol to give a clear solution. The initial pressure of gas was 1070 mm.; this fell gradually to 815 mm. The product was isolated by distillation in steam and extraction of the distillate with ether.

cyclo*Hexane*spirocyclo*hexane*, b. p. 208°/777 mm., is a clear, colourless, mobile liquid having a faint odour of geranium (Found : C, 86·7; H, 13·35. $C_{11}H_{20}$ requires C, 86·6; H, 13·3%). It is quite stable to permanganate and is only slowly dissolved by boiling, fuming nitric acid; bromine, in chloroform solution, is quite without action. The freshly distilled hydrocarbon has $d^{20·6°}$ 0·87833, n_C 1·47048, n_D 1·47313, n_F 1·47902, n_G 1·48398. Hence $[R_L]_D = 48·61$, $[R_L]_{F-C} = 0·75$, $[R_L]_{G-C} = 1·19$. The theoretical figures are 48·60, 0·74, 1·19, respectively. These values show no optical exaltation such as might be expected were the *cyclo*hexane rings in the *spiro*-hydrocarbon under a strain comparable with that in derivatives of *cyclo*butane, *cyclo*propane or *cyclo*heptane. Crossley and Renouf (*loc. cit.*) quote the following results, determined for 1 : 1-dimethyl*cyclo*hexane by W. H. Perkin, sen. :—$d^{15·5°}$ 0·78543, n_C 1·42958, n_D 1·43728, n_G 1·44203. Hence $[R_L]_C = 36·85$, $[R_L]_G = 37·78$, $[R_L]_{G-C} = 0·93$. The calculated figures are 36·78, 37·68, 0·90, respectively. The increase shown by the experimental figures over the theoretical is inappreciable.